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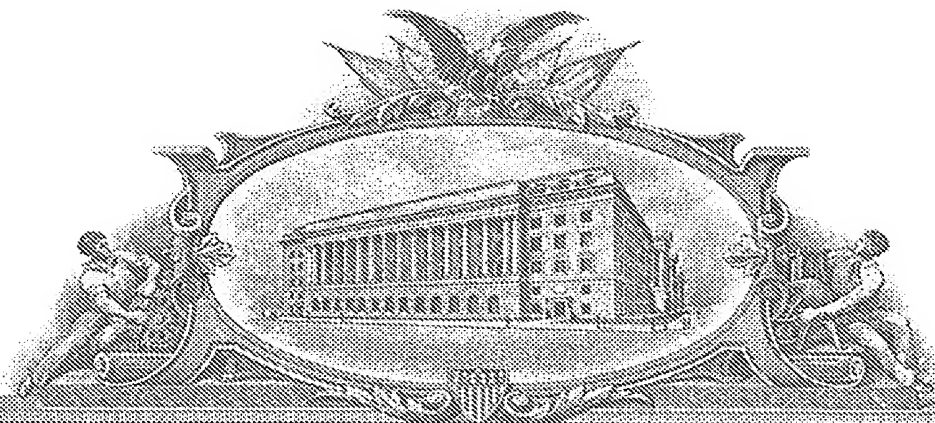
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**APPLICATION NUMBER: 10/803,502**

**FILING DATE: *March 17, 2004***

**RELATED PCT APPLICATION NUMBER: *PCT/US04/35452***

**THE COUNTRY CODE AND NUMBER OF YOUR PRIORITY APPLICATION, TO BE USED FOR FILING ABROAD UNDER THE PARIS CONVENTION, IS *US10/803,502***



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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

MAIL STOP PATENT APPLICATION  
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Transmitted herewith for filing is the patent application of:

Inventor(s): Brian Kevin Paul, Kannachai Kanlayasiri, Richard Dean Wilson and David  
Eli Alman

For: METHOD FOR MAKING DEVICES HAVING INTERMETALLIC  
STRUCTURES AND INTERMETALLIC DEVICES MADE THEREBY

Enclosed are:

- ☒ 53 pages of specification, 6 pages of claims, an abstract and a Combined Declaration and Power of Attorney (*unsigned*).
- ☒ 22 sheet(s) of drawings.
- ☒ Request for Non-publication and Certification under 35 U.S.C. § 122(b)(2)(B)(i).

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	Claims Filed	Number Free	Number Extra	Rate	Basic Fee
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Total Claims	45	20	= 25	\$9.00	\$ 225.00
Independent Claims	4	3	= 1	\$43.00	\$ 43.00
Multiple Dependent Claim Fee				\$145.00	
TOTAL FILING FEE					\$653.00

- ☒ Applicants claim the benefit of the earlier filing date of U.S. Provisional Application No. 60/455,735, filed on March 17, 2003. The entire disclosure of provisional application No. 60/455,735 is considered to be part of the disclosure of the accompanying application and is incorporated herein by reference.
- ☒ Assignee for this application is or will be The State of Oregon acting by and through the State Board of Higher Education on behalf of Oregon State University, and applicants request that this information be listed on the published application.

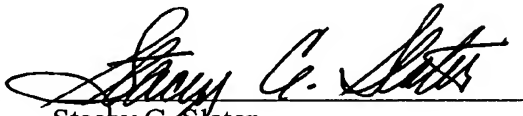
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PATENT

Express Mail No. EV339206216US  
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- ☒ Small entity status is claimed for this application.
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of: Paul et al.

For: METHOD FOR MAKING DEVICES HAVING INTERMETALLIC STRUCTURES  
AND INTERMETALLIC DEVICES MADE THEREBY

Examiner: Not yet assigned

Art Unit: Not yet assigned

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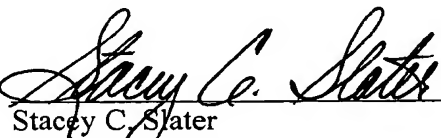
**REQUEST FOR NON-PUBLICATION AND CERTIFICATION UNDER**

**35 U.S.C. § 122(b)(2)(B)(i)**

This request is signed in compliance with 37 CFR § 1.33(b) and is submitted with the application **upon filing**. I hereby certify that the invention disclosed in the attached application **has not and will not be** the subject of an application filed in another country, or under a multilateral agreement, that requires publication at eighteen months after filing. I hereby request that the attached application not be published under 35 U.S.C. § 122(b).

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**METHOD FOR MAKING DEVICES HAVING INTERMETALLIC  
STRUCTURES AND INTERMETALLIC DEVICES MADE THEREBY****CROSS REFERENCE TO RELATED APPLICATIONS**

5       The present application claims the benefit of the earlier filing date of U.S. provisional  
application No. 60/455,735, filed on March 17, 2003, and is related to the subject matter  
disclosed in U.S. provisional application No. 60/253,683, filed on November 28, 2000, U.S.  
provisional application No. 60/253,609, filed on November 28, 2000, and U.S. utility  
application No. 09/996,621, now issued as U.S. Patent No. 6,672,502. These prior applications  
10   are incorporated in their entirety herein by reference.

**FIELD**

      The present invention concerns a method for making devices, particularly devices  
having an intermetallic structure that are useful as small energy and chemical systems, and  
15   devices made by the method.

**BACKGROUND****I.       Mecs Devices and Intermetallic Materials**

20       Microtechnology-based Energy and Chemical Systems (MECS) are devices that rely on  
embedded microstructures for their function. MECS devices are mesoscopic, i.e. in a size range  
between macro objects, such as automobile engines and laboratory vacuum pumps, and the  
intricate Microtechnology-based ElectroMechanical Systems (MEMS) sensors that reside on a  
chip. MECS devices typically, but not necessarily, have a length dimension ranging from about  
1 centimeter to about 20 centimeters, more typically from about 1 to about 10 centimeters.

25       Mesoscopic systems are expected to perform a number of important functions where a  
premium is placed on mobility, compactness, and/or point application. Internal processes of  
MECS devices operate on dimensional scales that are much smaller than traditional systems.  
For thermal and chemical applications, a small characteristic size provides the benefits of high  
rates of heat and mass transfer, large surface-to-volume ratios, and the opportunity for operating  
30   at elevated pressures.

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One subclass of MECS devices that is of great interest, both for research and industrial applications, comprises high-temperature microreactors and micro-scale heat exchangers. Potential applications for microreactors include: portable power packs that may extend the operating times of devices by a factor of ten or more; on-site neutralization of toxic chemicals, eliminating the need for transport and burial; miniaturized bioreactors that can enhance production of therapeutic drugs, or others that can detect toxic compounds; gasification of coals and heavy oils; flue gas desulphurization, and incineration of hazardous materials. Potential applications for micro-scale heat exchangers include: heat recovery for recycling waste heat; steam superheating for driving turbines; and recuperators for jet engines and diesel engines. These and other potential applications are discussed in U.S. patent application No. 09/369,679, "Microlamination Method for Making Devices," and U.S. patent application No. 60/095,605, "Methods for Making Devices by Component Dissociation and Microprojection Welding," which applications are incorporated herein by reference. Other features and applications pertinent to the present invention also are described in Paul, B.K., T. Dewey, D. Alman and R.D. Wilson, "Intermetallic Microlamination for High-Temperature Reactors," 4th Int. Conf. Microreaction Tech., Atlanta, GA, March 5-9, 2000, pp. 236-243 (American Institute of Chemical Engineers [AIChE]) incorporated herein by reference.

Heat exchangers are critical components in many systems. The performance of a heat exchanger can be improved at the micro-scale by increasing its surface-area-to-volume ratio. MECS fluidic devices increase the heat and mass transfer in heat exchangers using micro-scale features inside the devices. Many high temperature applications operate at temperatures above 600° C (Paul *et al.*, 2002). At these temperatures conventional materials for MECS devices, such as stainless steel, copper, and brass, do not function properly due to their inferior mechanical properties at high temperature (Jovanovic, 2001; Paul *et al.*, 2002). The work of D.W. Matson *et al.*, "Fabrication of Microchannel Chemical Reactors Using a Metal Lamination Process," Proc. IMRET3 (April, 1999, Frankfurt Germany), represents one such microreactor constructed of 316 stainless steel; another is the work of V. Hessel *et al.*, "High Temperature HCN Generation in a Complex Integrated Micro-reaction System," Proc. IMRET3 (April, 1999, Frankfurt Germany). At elevated temperatures of about 550°C and above,

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stainless steel has too low creep resistance, i.e., a high tendency to deform, to be generally suitable for many high-temperature microreactor applications.

Ceramics have been identified as a possible class of structural material for making microreactors suited to high temperature applications. See, M. Kim *et al.*, "The Fabrication of Flow Conduits in Ceramic Tapes and the Measurement of Fluid Flow through These Conduits,"  
5 Proceedings of the ASME Dynamic Systems and Controls Division, DSC V. 66, 1998. Ceramics have a very high melting point, low thermal conductivity and high corrosion resistance. But certain ceramic properties make them unsuitable for such applications. For example, sintered ceramics can sag, then shrink and/or warp during binder removal after the  
10 sintering process is complete. Furthermore, sintered ceramics have low fractional densities, which indicate high porosity.

Knitter *et al.* (1997), Winter and Knitter (1997), and Fischer *et al.* (1999) developed micro reactors and micro pumps, from ceramic materials such as  $\text{Al}_2\text{O}_3$ , AlN and electroconductive  $\text{Al}_2\text{O}_3/\text{TiN}$ . Microfabrication techniques such as micro molding were used to  
15 shape these materials. These authors describe an  $\text{Al}_2\text{O}_3$  micro reactor having a channel cross section of  $500 \times 500 \mu\text{m}^2$  made, as well as a micro pump having a  $200 \mu\text{m}$  channel width and a  $1000 \mu\text{m}$  channel height.

Spadaccini *et al.* (2002) used silicon wafers to build a micro combustor for a micro gas turbine engine. The engine was fabricated from six pieces of etched silicon wafers by fusion  
20 bonding. Stack thicknesses prevented bonding when two three-wafer stacks were bonded. However, adding wafer piece-by-piece to the first three-wafer stack provided a decent bond quality to most of the wafers.

Micro devices produced from ceramics have faced dimensional instability problems such as sagging, porosity, and volumetric shrinkage, and building micro devices from silicon is  
25 not suitable for MECS applications due to its high thermal conductivity (Peterson, 1998; 1999; Paul *et al.*, 2002).

Intermetallics have material properties more desirable than those of the previously discussed materials, such as high melting point, low thermal conductivity, and good corrosion resistance. In particular, metal aluminides are known for their resistance to high temperature  
30 oxidation (Pope and Darolia, 1996) as a result of an inherent property of the aluminum (Al)



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contained in the aluminides to form protective oxide layers ( $\text{Al}_2\text{O}_3$ ). Aluminides of nickel (Ni), such as  $\text{Ni}_3\text{Al}$  and  $\text{NiAl}$ , are aluminides that currently are of interest in (MECS) device fabrication. Hence, both of these nickel aluminides have become promising structural materials in the building of MECS devices such as heat exchangers and chemical reactors (Paul *et al.*, 2000; Alman *et al.*, 2001; Paul *et al.*, 2002). Compared to the candidate  $\text{Ni}_3\text{Al}$ , however,  $\text{NiAl}$  forms a protective oxide layer because of its higher aluminum content. Moreover,  $\text{NiAl}$  also has a higher melting temperature than  $\text{Ni}_3\text{Al}$  (Jovanovic *et al.*, 2001). Stoichiometric  $\text{NiAl}$  has the highest melting temperature among the intermetallic compounds of the Ni-Al system. In addition,  $\text{NiAl}$  has a lower density, and higher Young's modulus.

According to the binary phase diagram for Ni-Al systems, five possible nickel aluminide intermetallic phases could be found in an Ni-Al system –  $\text{NiAl}_3$ ,  $\text{Ni}_2\text{Al}_3$ ,  $\text{NiAl}$ ,  $\text{Ni}_5\text{Al}_3$ , and  $\text{Ni}_3\text{Al}$ . The  $\text{NiAl}$  phase is different from other typical intermetallic compounds in that it has large deviations from the stoichiometric ratio while the other intermetallic compounds are either line compounds or have very small deviations. The stoichiometric composition for  $\text{NiAl}$  is 50 atomic percent (at%) of Ni and 50 at% of Al, with compound deviations ranging from 45 to 59 at% of Ni (at 400° C). These deviations provide flexibility in producing the  $\text{NiAl}$  intermetallic. However, intermetallic properties change with composition deviations, for instance a decrease in the melting point from the stoichiometric melting temperature.

Material properties of stoichiometric  $\text{NiAl}$  are provided by Table 1 below.

Melting Point	1638 °C
Density	5.86 g/cm <sup>3</sup>
Young's Modulus (At Room Temperature)	188 GPa
Thermal Conductivity (Temp. Range 20-1100 °C)	70-80 W/m°C
Coefficient of Thermal Expansion (Temp. Range 820-1560 °C)	15.1x10 <sup>-6</sup> °C <sup>-1</sup>

Table 1

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However, NiAl has two material properties that are problematic for MECS development: its brittleness at room temperatures; and low strength and creep resistance at high temperatures. NiAl is hard and brittle at room temperature, and is very difficult to form using traditional machining techniques. The brittle-to-ductile-transition temperature (BDTT) of NiAl ranges from 277° C to 727° C depending upon compositions of the compound, and the ductility of the material is dramatically improved at temperatures above 600° C (Liu and Kumar, 1993; George *et al.*, 1994). These numbers indicate the requirement of high temperature fabrication for NiAl intermetallics. Nevertheless, there is no clear guidance in selecting alloying elements to improve room temperature ductility of NiAl. The selection of these elements has been based on empirical findings.

Wang *et al.* (1998) showed the feasibility of using the LIGA process to build intermetallic, high-aspect-ratio microstructures from electroplated nickel and aluminum. Intermetallic micro posts of nickel (Ni) and aluminum (Al) were fabricated by co-depositing micron-sized Al particles during Ni plating. The intermetallic posts of nickel aluminide (Ni<sub>3</sub>Al) with a 200  $\mu$ m diameter and a 500  $\mu$ m height were obtained after annealing at 630° C for 780 minutes.

## II. Foils for Making Devices

Foil is a useful material form for building MECS devices using a lamination bonding techniques. Typical foil thicknesses that have been used to make MECS devices range from 25 to 250  $\mu$ m; however, thinner or thicker foils have been used as well (Martin *et al.*, 1999). To date, only Ni<sub>3</sub>Al intermetallic foil of thicknesses close to this range are available (Demura *et al.*, 2000; 2001). Most intermetallic foils of such thicknesses cannot be formed by traditional material processing techniques, such as cold rolling, because of their brittleness.

Methods for making nickel aluminide foils by non-traditional material processing techniques have been researched. Alman *et al.* (1995) developed a metal processing technique to synthesize intermetallic foils from elemental Ni and Al foils through self-propagating, high-temperature synthesis reactions. This process used reactive diffusion between Ni and Al to produce the foils and consisted of two major processing steps named "Reaction Initiation" and "Post-Reaction Thermal Aging," respectively. The thickness of each elemental foil ranged from

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50 to 250  $\mu\text{m}$ . Elemental Ni and Al foils were stacked in an alternating sequence and then heated in a vacuum environment at 620° C for an hour to initiate the reaction between the foils. The temperature was then increased to 700° C and held at this temperature for 15 minutes to ensure that the Al was completely consumed into the Ni matrix. In the second step, the specimen was annealed at 800° C for an hour under applied pressure of 20 MPa to equilibrate the intermetallic phases and to close the remaining voids in the foil. The major final intermetallic phase presented was  $\text{Ni}_2\text{Al}_3$  when the specimen was heated at 950° C for 50 hours. The main intermetallic phase found was  $\text{Ni}_3\text{Al}$  when the sample was annealed at 1100° C. In both cases, unreacted Ni remained in the foils after the annealing process.

Alman *et al.* (1996) proposed another processing technique to produce nickel aluminide foils from elemental foils. The Ni foil thickness was 25  $\mu\text{m}$ , and the Al foil thickness varied from 125 to 500  $\mu\text{m}$ . The process began with stacking elemental Ni and Al foils in an alternating sequence. The stack of foils was then bonded in a vacuum hot press at bonding conditions of 600° C, 10 MPa applied pressure, and 2 hours bonding time. The major intermetallic phase after this step was NiAl with an additional percentage of  $\text{NiAl}_3$ . The specimen was annealed at 450° C for either 1, 10, or 100 hours to allow intermetallic phases to equilibrate. The final intermetallic phase presented in the foil was  $\text{NiAl}_3$  with remaining pure Al.

Raviprasad and Umemoto (1996) cold rolled layered structures of aluminum-metal systems, including an aluminum-nickel system. Aluminum sheets with thicknesses of 80  $\mu\text{m}$  were alternatively stacked with 80- $\mu\text{m}$ -thick nickel sheets. Before rolling into a desired thickness, the stack of materials was heat treated at 500° C for 6 hours under a 1 kilogram load. During rolling, the number of layers was doubled at every pass by cutting the sample and stacking onto the other half. After cold rolling, a good adhesion between these two materials was obtained, and no intermetallic phase was detected by X-ray diffraction unless the composite sheet was heat treated. After heat treatment at 500° C for 8 hours, the intermetallic phase was  $\text{NiAl}_3$  in addition to the starting elements.

Battezzati *et al.* (1999) attempted to use a cold rolling process to produce NiAl foil. An aluminum foil with a thickness of 120  $\mu\text{m}$  was rolled into an 80  $\mu\text{m}$  thick nickel foil to provide the desired stoichiometric composition. The foils were rolled and folded until either the desired

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thickness was achieved or the foils had noticeable mechanical failure. After cold rolling, none of the intermetallic phases of Al-Ni system was detectable. The rolled foils were then annealed at various conditions. NiAl was the main composition of the foils when they were rolled with a high number of passes (60-70 passes) and annealed at 700° C. However, other intermetallic phases, such as Ni<sub>2</sub>Al<sub>3</sub> and Ni<sub>3</sub>Al, along with remaining Ni, also were present in the foils.

Demura *et al.* (2001) used a cold rolling process to fabricate intermetallic Ni<sub>3</sub>Al foils having thicknesses of 57 to 315  $\mu$ m, which was previously considered impossible. The floating zone solidification technique was the key to success. By using this solidification technique, ductile Ni<sub>3</sub>Al rod was produced. After cutting into a sheet, the Ni<sub>3</sub>Al sheet was cold rolled into the desired thickness.

Although several efforts have been made to produce nickel aluminides foils, none has reported production of homogeneous NiAl foils. Further, foil flatness, which is important in fabricating MECS devices, is difficult to obtain from manufacturing process such as cold rolling. NiAl foils are useful for making MECS devices. An approach for producing NiAl foils having requisite dimensional stability, flatness and desired composition, which are important factors in producing MECS devices, therefore is required.

It would be advantageous to be able to form MECS devices from intermetallics, and thus make use of high-temperature properties of intermetallics. However, to date this has proved virtually impossible because intermetallics are too brittle and therefore are poor substrates for facile machining and forming at room temperature.

### III. Reactive Diffusion

Diffusion bonding of dissimilar materials has been of interest to many researchers (Philibert, 1991; Kao and Chang, 1993; van Loo *et al.*, 1997; Paransky *et al.*, 1999). The kinetics of the process results mainly from two sub-processes: chemical reactions at interfaces between two dissimilar metals; and diffusion of chemical species. The processes involving these two steps are usually called reactive diffusion. At the beginning of the process, interfacial chemical reactions take place and lead to the nucleation and growth of intermediate phases. After that the atoms of the diffusion couple diffuse across the intermediate phases and then

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chemically react with the surface atoms to form more intermediate phases. The intermediate phases are grown in this fashion until the elemental materials are consumed.

The solid-state growth of the intermetallic layer between the two elementary substances, Ni and Al, at a certain temperature and pressure results from the above two sub-  
5 processes. Once the bonding surfaces are in intimate contact, atoms of Ni and Al on the contacting surfaces react and form a thin layer of NiAl intermetallic. After that, Ni and Al atoms diffuse across the NiAl layer and react at the interfaces to the surface Al and Ni atoms, respectively. The NiAl compound continues to form in this manner until the elemental foils are depleted.

10 When dissimilar solid-state materials with different diffusivities diffuse into each other, such as in the reactive diffusion between Ni and Al, voids can be formed in the starting material that has more rapidly diffusing species. This phenomenon is called the Kirkendall effect. Based on the vacancy mechanism of diffusion, for a diffusion couple, porosities occur in the higher-diffusivity material because its atoms move to fill vacancies at a higher rate than that of  
15 the other material.

For nickel and aluminum, nickel diffusion is dominant at high temperatures (1,000-1,400° C) while aluminum is the dominant diffusing species at lower temperatures (Mehrer, 1990; d'Heurle, 1992). These findings are supported by a study of Colgan (1990) in the diffusion of thin film of Ni and Al. The formation of the most Al-rich phase ( $\text{NiAl}_3$ ) takes place  
20 at the lowest temperature and the most Ni-rich phase ( $\text{Ni}_3\text{Al}$ ) grows with increasing annealing temperature. However, these findings contradict later literature. According to an investigation of Michaelson *et al.* (1996) on reactions in Ni-Al thin film, NiAl is the first intermetallic phase that forms in a Ni-Al system at low temperatures (87 – 217° C). If the starting elements are not completely consumed by NiAl formation, the most Al-rich phase,  $\text{NiAl}_3$  is produced.

25

#### IV. Bonding Intermetallic Compounds

Bonding intermetallic compounds has been studied by many researchers. Joining techniques, such as diffusion bonding, diffusion brazing, and transient liquid phase bonding, were found promising for bonding of intermetallic compounds. Nakao *et al.* (1991) join  
30 intermetallic rods of TiAl (Ti-38mass%Al) in a vacuum using solid-state diffusion bonding.

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The results from their study created a diffusion bonding diagram that showed ranges of bonding temperatures, pressures, and times that were able to produce a decent bond without interfacial voids. The feasible ranges were 10 – 30 MPa for the bonding pressure, 927 – 1227° C bonding temperature, and 1000 – 4000 seconds bonding time.

5 Glatz and Clemens (1997) showed that solid-state diffusion bonding can be used to join intermetallic sheets of TiAl (Ti-47Al-2Cr-0.2Si). Void-free joints of this material were produced at a temperature of 1,000° C in the range of 20-40 MPa bonding pressures, and 1-3 hours bonding times in a vacuum.

Uenishi *et al.* (1995) used diffusion brazing with aluminum foil (99.9% pure) as filler  
10 metal to join TiAl (Ti-34mass%Al). Specimens bonded at 900° C, under 30 MPa bonding pressure for 64 minutes with subsequent heat treatment at 1,300° C for 64 minutes provided a joint that had the same tensile strength as that of the parent material. Both processes were conducted under vacuum.

Moore and Kalinowski (1993) joined NiAl intermetallic rods using diffusion brazing  
15 combined with hot isostatic pressing. The filler metal was self-generated by evaporating Al from the specimen surfaces to form a thin Ni-rich layer. This was accomplished by heating the NiAl specimens at 1,530-1,570° C for 1-3 minutes. After cooling to room temperature, the specimens were then brazed at 1,530-1,570° C for 1-15 minutes under slight pressure of 0.011-0.032 MPa. The specimens were then hot pressed at 1,340° C and 138 MPa for 4 hours. After  
20 that the specimens were heat treated at 1,530° C for 6 hours to homogenize the chemical compositions. All operations in this study were performed in a vacuum environment.

Strum and Henshall (1994) used liquid-assisted diffusion bonding to join NiAl. High  
purity Ni and Al were deposited by electron beam evaporation onto the joining surfaces with  
0.66 to 1 thickness ratio of Ni to Al to provide stoichiometric NiAl after bonding. The coated  
25 specimens were then placed in contact at 1,200° C for 1-32 hours in an argon atmosphere to homogenize the chemical compositions.

Wu and Huang (2001) used laser-assisted superplastic forming and diffusion bonding to  
join TiAl intermetallic alloy (Ti-45Al). The laser was used to produce a layer of fine grain  
structure on the bonding surfaces to achieve the superplastic bonding at a lower temperature and  
30 a shorter time. The laser used in the experiment was a HGL-84 CW CO<sub>2</sub> laser at 2 kW,

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scanning rate 10 mm/s, and defocus distance 32 millimeters. The laser-treated specimens provided a sound bond within a temperature range of 900° C -950° C, 60 MPa, and 1 hour bonding time in an argon atmosphere.

5 1. Bonding Temperature

For diffusion bonding, temperature is a critical process variable because the diffusion mechanism of atoms is significantly dependent on the temperature. The high sensitivity of the diffusion mechanism to the temperature could be explained by the kinetic theory of the diffusivity of atoms. According to Reed-Hill and Abbaschian (1991), the diffusion coefficient of atoms can be expressed as a function of temperature as:

$$D = D_0 e^{-Q/kT}$$

where  $D$  is the diffusion coefficient of an atom at temperature  $T$ ,  $D_0$  is a constant,  $Q$  is the activation energy of diffusion,  $k$  is Boltzmann's constant, and  $T$  is the absolute temperature. From this expression, the diffusivity,  $D$ , varies exponentially with temperature. Thus, only small variations in temperature produce large changes in the process kinetics. Since the diffusion of atoms is a thermally induced process, it is reported that the temperature at which diffusion bonding starts to occur is generally above half the absolute melting temperature ( $T_m$ ) of the most fusible bonding metal (Schwartz, 1979).

To obtain good diffusion bonding for metals, Kearns (1980) recommended a bonding temperature between 0.6 and 0.8 $T_m$  while Derby and Wallach (1982), Nakamura *et al.* (1988), and Hill and Wallach (1989) suggested a temperature in the range of 0.5 - 0.8 $T_m$ . Dunford and Partridge (1992) used 0.5 $T_m$  as the lower limit of bonding temperature, but did not state an upper temperature limit. Kazakov (1985) suggested the bonding temperature be anywhere between 0.5 and 0.7 $T_m$  and recommended the optimal temperature for diffusion bonding to be 0.7 $T_m$ . However, to avoid undesired phase transformations and large deformations of the materials, a diffusion bonding process is recommended to operate under as low temperature and low pressure as possible (Orhan *et al.*, 1999).

In addition, temperature also plays an important role in the first stage of diffusion bonding. Since the yield strength of material is a function of temperature, the strength of

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surface asperities decreases as the bonding temperature increases. Thus, high temperature assists plastic deformation of the surface asperities.

## 2. Applied Pressure

5 According to the diffusion bonding mechanisms, it is clear that pressure is a major factor in initiating the first stage of diffusion bonding. Kazakov (1985) concluded the roles of applied pressure in diffusion bonding as follows:

1. Breaking the surface oxide film and contaminants and plastically deforming asperities on the mating surfaces;
- 10 2. Enhancing atomic interaction by bringing intimate contact between the bonding surfaces; and
3. Activating the subsequent bulk processes of the bonding material such as diffusion and recrystallization.

Given these effects, the main purpose of the applied pressure is to produce plastic  
15 deformation leading to maximum contact area between the mating surfaces. If two metallic specimens brought into contact have ideally smooth, clean and parallel surfaces, metallic bonds will form and no external energy input is required (Garmong *et al.*, 1975). However, these ideal surfaces are difficult to achieve in practice. Therefore, in a real diffusion bonding process, if the applied pressure and bonding temperature are not high enough and cannot provide plastic  
20 deformations of the surface asperities, diffusion bonding will not take place.

## 3. Bonding Time

In a diffusion bonding process, bonding time should be minimized because of metallurgical and economical considerations. The bonding time should be just long enough for  
25 the diffusion processes to complete, which is indicated by no remaining void at the bond interface. The strongest joints are generally formed when intimate surface contact has been established and diffusing atoms have just moved across the joint interface (Alm, 1970). In practice, to obtain a sound bond, bonding times can be varied from a few minutes to several hours depending upon the bonding materials (Hill and Wallach, 1989; Orhan *et al.*, 1999).  
30 Increased bonding time improves bond strength up to a certain point. Further bonding decreases bond strength due to grain growth (Kazakov, 1985). The bonding time can be



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reduced by increasing the applied pressure. For instance, in diffusion bonding of Ti-6Al-4V, the bonding time can be reduced by a factor of three if the bonding pressure is increased by a factor of ten (Pilling, 1988).

5

#### 4. Surface Finish

Surface finish is another parameter that greatly influences the bond quality of diffusion-bonded joints since it involves all bonding mechanisms in the process. Surface finish features include roughness, waviness, flatness, flaws, and lay. Only surface roughness and waviness have been found to play an important role in diffusion bonding mechanisms. Surface roughness is fine random irregularities of a surface that is usually caused by production, tool-related actions such as a milling tool or grinding wheel. Surface waviness is a more widely spaced, repetitive deviation than surface roughness and usually occurs due to an individual machine factor, such as machine vibration, or spindle deflection and imbalance (Nicolls, 1974). Surface roughness is superimposed over surface waviness.

15

Surface finish was found to affect shear strength of diffusion bonded joints. Under the same bonding conditions, joints with rougher bonding surfaces provided lower shear strengths than joints with finer surfaces. The rougher surfaces needed more extreme bonding conditions to obtain the same joint quality as that of the finer surfaces (Ridley *et al.*, 1992). The surface roughness of the bonding surfaces also affects the bonding time. It is substantially dependent on the size and shape of interfacial voids, which are determined by the surface roughness. Islam *et al.* (1997), and Islam and Ridley (1998) found that bonding time was reduced by decreasing surface roughness. Under a given pressure and temperature, the wavelength of the surface roughness is the most influential factor in determining the bonding time. With a constant amplitude of surface roughness, bonding time increases with the wavelength of the surface roughness (Pilling *et al.*, 1996).

20

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#### SUMMARY

Embodiments of a method and apparatus for making an intermetallic device, or a device having at least an intermetallic component, are described. One embodiment of the method comprises making an intermetallic structure from laminae having one or more layers comprising substantially pure metals. Laminae are patterned to provide features, shapes, etc., which

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collectively define a desired structure, by machining, lithography and etching, or other patterning technology. A lamina can be patterned because at least that portion of the lamina that must be patterned comprises a patternable metal or alloy. In some embodiments, each of the layers of the lamina comprised substantially pure, patternable metal or metal alloys, which are patternable. Patterned, and possibly non-patterned laminae, are then stacked and registered in the order needed to create the final monolithic intermetallic structure. The stack of registered, patterned laminae is then processed to form a monolithic, intermetallic structure. Patterning lamina or laminae prior to making the intermetallic eliminates the need to pattern intermetallic compounds, which typically are (1) difficult to roll into sheets of the preferred thickness range for micro-reactor applications, and (2) difficult to pattern, as intermetallics tend to be brittle at room temperature.

For those intermetallics capable of being rolled into sheets from, for instance, from directionally solidified intermetallic ingots, and then patterned through means such as lithography and chemical etch, monolithic intermetallic structures can be formed from intermetallic blank layers, particularly homogeneous (single phase composition materials) layers, that have been machined and/or otherwise patterned. The layers are then stacked and registered. The stack is subsequently bonded by a process, such as diffusion bonding, to form a monolithic intermetallic structure. This process may not be feasible for all intermetallics, such as NiAl, because there currently is no method known for rolling such materials to form foils.

Monolithic intermetallic structures may be formed with different internal geometries, topologies and/or topographies, thereby allowing for different applications. Because of their properties, including high melting temperature, high (or low) thermal conductivity (depending on the intermetallic), and high corrosion resistance, intermetallics are excellent candidates for microreactors. Applications include portable fuel cells; chemical detoxification apparatuses for environmental purposes; on-site neutralization of toxic chemicals; miniaturized bioreactors for production of pharmaceuticals; and toxic substance detection apparatuses. In addition, intermetallics are excellent materials for making high-temperature micro-scale heat exchangers. Monolithic intermetallic structures can contain catalysts that promote specific chemical reactions, such as that needed to produce hydrogen in a fuel cell. Monolithic intermetallic structures may be fabricated so as to contain microscopic internal features, or macroscopic

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internal features, depending on the application, according to embodiments of the present invention.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

- 5           FIG. 1 is a block diagram illustrating one embodiment of a disclosed method for making a monolithic intermetallic structure.
- FIG. 2 illustrates the formation of one embodiment of a lamina blank.
- FIG. 3 illustrates examples of patterned laminae.
- FIG. 4 illustrates a set of ordered patterned laminae to be stacked.
- 10          FIG. 5 illustrates a set of patterned laminae stacked in a registration jig.
- FIG. 6 illustrates a set of patterned laminae stacked and aligned in pairs.
- FIG. 7 illustrates tack bonding stacked, registered and patterned laminae.
- FIG. 8 illustrates a catalyst fixed to the surface of an inner feature of a monolithic structure, such as an intermetallic structure.
- 15          FIG. 9 illustrates a catalyst positioned on a support within a monolithic structure.
- FIG. 10 illustrates a catalyst embedded in a surface of an internal feature of a monolithic structure.
- FIGS. 11A, B illustrate a lamina stack with posts bridging plural laminae.
- FIG. 12 illustrates a monolithic structure with posts bridging plural laminae.
- 20          FIG. 13 illustrates a monolithic structure with cylindrical features.
- FIG. 14 illustrates a monolithic structure defining an aperture having a variation in cross-sectional area.
- FIG. 15 illustrates a monolithic intermetallic structure defining a well, holding e.g., catalytic material, adjacent a flow-through aperture.
- 25          FIG. 16 illustrates a monolithic structure having multiple input/output ports and plural flow apertures.
- FIG. 17 is a schematic diagram of laminae used to evaluate factors influencing registration and buckling of laminae during thermally enhanced edge registration.
- FIG. 18 is a schematic view of one embodiment of a registration fixture used for
- 30          thermally enhanced edge registration.

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FIG. 19 is a graph of misalignment (microns) versus allowance between fixture and laminae at processing temperatures (microns).

FIG. 20 is a schematic depiction of laminae used to produce a Ni<sub>3</sub>Al intermetallic counterflow heat exchanger.

5 FIG. 21 is a schematic illustrating geometry, order, composition and cross-sectional profile of patterned foils and filler metal for a fin of a microchannel.

FIG. 22 illustrates lamina designed to form a parallel flow heat exchanger.

FIG. 23 is graph of volumetric flow rate versus pressure drop (psi) showing pressure drop test results for NiAl microchannel arrays.

10 FIG. 24 is a cross section of a microchannel array serving as a control to establish reduced fin warpage in microchannel arrays made according to one embodiment of a process according to the present invention.

FIG. 25 is a cross section of a microchannel array showing reduced fin warpage in microchannel arrays made according to an embodiment of a process according to the present invention relative to the process used to make a similar device as illustrated by FIG. 24.

15 FIG. 26 is a micrograph of two 100:1 aspect ratio microchannels having about a 125 micron channel height formed between three alternating NiAl fins illustrating the ability to control warpage and dimensions on the fins of a microchannel array.

FIG. 27 is a graph of atomic percent ratio of Al to Ni in a fully developed NiAl foil.

20 FIG. 28 is a cross section at 8X of a leak-tight 28:1 aspect ratio NiAl microchannel array device having a microchannel height of about 135 microns and about 20 to 30 microns warpage per fin over a span length of 3.81 millimeters.

## DETAILED DESCRIPTION

### 25 I. Methods for Making Structures that Include an Intermetallic

FIG. 1 is a block diagram illustrating certain procedures of one embodiment of a disclosed method used to make a monolithic intermetallic structure. Block 102 concerns selecting materials useful for making a desired structure. Starting materials may comprise any metals, preferably metals selected from the group including, but not limited to, aluminum,  
30 nickel, titanium, molybdenum, tantalum, copper, gold, silver, lead, tin, iron, antimony,

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magnesium, manganese, bismuth, germanium, and tungsten. Binary compounds, such as binary alloys and intermetallics (e.g., metal aluminides such as NiAl), and ternary compounds (e.g., metal aluminides having a formula  $M^1_{1-x}M^2_xAl_1$ , such as FeNiAl-type compounds) comprising these metals can be used as well. Alloys and intermetallics may be used as purchased  
5 commercially, if available, with or without additional processing, or formed as a part of the process described herein, such as through the production of NiAl from elemental nickel and aluminum.

In block 104, a typical lamina blank is formed from one or more metal, alloy or intermetallic layers. A "layer" comprises a sheet of material that may be of any thickness, but  
10 generally has a thickness of 32 mm or less, and more typically from about 0.025 to about 0.100 mm. Sheets of non-uniform thickness also can be used.

Structures are referred to as lamina blanks if they have not yet been "patterned," i.e., they have not been changed geometrically, topographically or topologically. The layers may be used as formed or purchased, but typically are initially surface-prepared. "Surface-prepared"  
15 generally refers to removal of foreign substances, such as grease and dirt, from a surface, and removing surface metallic compounds, such as metal oxides, that can potentially interfere with bonding and intermetallic reactions. Surface-prepared layers are stacked in a pre-selected order, and bonded, typically by applying pressure and heat, in a manner effective to form a single lamina blank having distinguishable layers.

One aspect of the disclosed embodiments comprises forming an intermetallic while  
20 practicing the method, such as during a heated bonding step. To make a uniform intermetallic structure from multiple laminae, each lamina blank typically comprises the same starting metals. To make a non-uniform intermetallic structure, the constituent lamina blanks may be varied as to, for example, number of layers, the relative amount of material, e.g., by varying the  
25 volume of one layer relative to another, and/or chemical composition of each layer. In working embodiments directed to making the intermetallic during process steps used to also make a device, or component thereof, by microlamination each of the layers of a lamina blank comprised one substantially pure single metal.

The composition and the thickness of a particular lamina also can be determined by  
30 judicious selection of the constituent elemental materials, and relative volume of such materials.

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For example, nickel and aluminum foils can be used to form a NiAl lamina having a particular thickness and a particular Ni:Al stoichiometry. Again by way of example, to provide a 1:1 atomic ratio of nickel to aluminum, the constituent nickel and aluminum foils are selected to have dimensions that provide a 2:3 volumetric ratio of nickel-to-aluminum. Thus, the lamina  
5 thickness and molecular composition can be selected by proper selection of a volumetric ratio of constituent elemental foils or layers.

However, if an intermetallic blank (a non-patterned raw material from which a lamina is patterned, and can be in a sheet form referred to as a foil) is patternable by, for instance, machining, pressing, folding, twisting, shrinking, stretching, deforming, and combinations  
10 thereof, that intermetallic compound may be formed into a layer for inclusion in a lamina or laminae that are to become part of the final monolithic structure. Methods for making and processing single crystal intermetallics are now becoming known. Foils of single-crystal intermetallics have been patterned and used to make devices, one embodiment of which is described in Example 7. For example, Ni<sub>3</sub>Al has been made by cold rolling. See, for example,  
15 Demura *et al.*, "Ductile Thin Foil of Ni<sub>3</sub>Al," Mechanical Properties of Structural Films, (2000), which is incorporated herein by reference. Example 4 provides additional detail concerning a method for making a thin foil of a single crystal of Ni<sub>3</sub>Al.

One benefit of the disclosed embodiments for making devices using such single-crystal materials is the ability to produce a high temperature microchannel device with intricate internal  
20 features from a normally brittle material. The single crystal material can be converted to a polycrystalline material during heating and/or pressure application involved with the microlamination process. Thus, the single crystal material can be patterned to form laminae. Single crystal laminae are bonded together and can be converted, if desired, to a polycrystalline material to obtain, for example, a complex microscale device with internal features.

25 In block 106 lamina blanks can be patterned. "Patterning" means changing the lamina blank from its initial geometric shape, topology, topography, or combinations thereof. For example, patterning may include, but is not limited to, formation of apertures or channels, such as by removing material through machining, making deviations in or from planarity (such as curved surfaces), and formation of geometric shapes, such as cylindrical, spherical, polygonal,  
30 and conical. Patterning techniques include, but are not limited to, machining, pressing, folding,

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twisting, shrinking, stretching, deforming, and combinations thereof. Machining techniques include, but are not limited to, laser ablation (both 266 and 532 nm lasers have been used with working examples.), chemical etching, lithographic techniques, plasma etching, mechanical abrasive flow methods, such as particle beams and sand blaster, high pressure hydraulic cutters, electromechanical or electrochemical methods, ultrasonic techniques, electromagnetic means including momentum transfer and energy transfer from any portion of the electromagnetic spectrum, including X-rays and gamma rays, wire and ram electrodischarge machining (EDM), waterjet and abrasive waterjet, precision plasma cutting, and combinations thereof, or other machining means commonly known to persons of ordinary skill in the art.

In block 108, the patterned laminae are fixed relative to one another, such as by being stacked and registered. "Registering" or "registration" generally refers to orienting and/or aligning two or more objects, such as laminae, or features on adjacent lamina, such as apertures, channels, etc., with respect to one another. Registration may be accomplished mechanically using a registration jig. Alternative methods of registering the laminae include, but are not limited to, an interferometer utilizing laser, ultrasound, light, microwave, or other wave source, alignment tools utilizing one or more of mechanical, electrical, electromagnetic, acoustic, and particle beam techniques, and combinations thereof.

A particularly useful technique for registering plural laminae for microlamination has now been developed, and is referred to as thermally enhanced edge registration (TEER).

Differences in the thermal expansion of laminae relative to a fixture are used to produce a registration force on the laminae at the bonding temperature. Plural laminae are positioned properly on a fixture having a smaller coefficient of thermal expansion than the material used to make the laminae. At room temperature, a clearance allowance allows the laminae to be positioned easily on the fixture. At an elevated temperature, the laminae have expanded more than the fixture. The laminae therefore contact the edge of the fixture, or pins on the fixture, thereby producing a registration force.

The clearance required for a particular registration process can be calculated. When heated, the device expands, and its new length is provided by Formula 1:

$$L_2 = L_1 + \delta L_1 = L_1(1 + \alpha_1 dT)$$

**Formula 1**

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The slot in the fixture also expands, and the new width is provided by Formula 2:

$$L_4 = L_3 + \delta L_3 = L_3(1 + \alpha_2 dT)$$

**Formula 2**

With reference to Formulas 1 and 2,  $L_1$  = the device length before thermal expansion;  $L_2$  = the  
5 length subsequent to expansion;  $L_3$  = the width of the slot in the embodiment of the fixture used  
before thermal expansion;  $L_4$  = the width of the slot subsequent to thermal expansion;  $\alpha_1$  =  
coefficient of linear thermal expansion for the laminae material;  $\alpha_2$  = the coefficient of linear  
thermal expansion for the fixture material; and  $dT$  is the difference in bonding and room  
temperature.

10 For TEER, the expanded device length and the expanded width of the fixture slot  
should be substantially the same so that the laminae edges contact the boundary, and the thermal  
registration force is applied to the laminae edges. Thus,  $L_2 = L_4$ . The width of the slot therefore  
is provided by Formula 3:

$$L_3 = L_2 / (1 + \alpha_2 dT) = L_1 (1 + \alpha_1 dT) / (1 + \alpha_2 dT)$$

15 **Formula 3**

Examples 1 and 2 provide further detail concerning the TEER process.

In block 110, certain of the stacked and registered laminae may be fixed relative to one  
another, such as by being tack-bonded together, rendering the laminae fixed in position with  
respect to one another. Tack-bonding can be done over the entire surface of the laminae, or  
20 only at selected regions, such as at the outer edges, or at various regions on the surfaces of the  
laminae. Tack-bonding preferably is accomplished using adhesives, such as cyanoacrylate,  
which are combusted during processing. Fixing laminae relative to one another also can be  
accomplished using TEER.

In block 112, the lamina stack is converted, generally by heating, to a monolithic  
25 structure, which may be wholly intermetallic, or may comprise an intermetallic portion.  
Heating may be done at a temperature sufficient to form the desired intermetallic, such as from  
about 500°C to about 1100°C for the disclosed embodiments. And, heating may be  
accomplished by any suitable method, such as through conduction, convection, radiation with  
electromagnetic waves through the use of electrical resistance, inductive heater, laser or other  
30 sources of electromagnetic waves, acoustic waves, particle beam bombardment, mechanical



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means, or other means commonly known to persons of ordinary skill in the art. Heating may occur in an atmosphere of reduced pressure and/or inert gas atmosphere.

Without being limited to theories of operation, conversion to an intermetallic may occur through liquid phase bonding, wherein at least one of the metals becomes liquified and diffuses into the other adjacent metals. In such a case, care must be taken to minimize the initial clamping force used to fix the laminae relative to one another. Too much initial pressure can break native oxide coatings (especially in the case of aluminum) on the outside of the metal, which prohibits the liquid phase from losing shape. Once the liquid phase has been completely absorbed, the pressure may be increased for final diffusion bonding to eliminate voids in joints between laminae. For 25 mm x 25 mm device sizes, initial clamping pressures for NiAl formulations generally less than 50 psi at 1000°C, more typically from about 1 to about 10 psi, in order to avoid breaking native oxide bonds. Typically it has been found that for NiAl formulations, most of the liquid has been absorbed by the fourth hour of a 10 hour bonding cycle.

Conversion to an intermetallic also may occur through solid-state diffusion bonding, wherein the temperature of the stack is less than the melting temperature of any of the metals within the stack, but the temperature is sufficient to facilitate diffusion, which occurs among layers in intimate contact with adjoining layers. Conversion to an intermetallic also may be accomplished through other mechanisms of bonding known to persons of ordinary skill in the art.

FIG. 2 shows one embodiment of a lamina blank 205. In general, a lamina may comprise any number of layers, and may be a planar or a non-planar shape, i.e., curved, such as cylindrical, spherical, saddle-shaped, conical, hemispherical, or, in general, any non-planar shape. In the embodiment illustrated by FIG. 2, three layers comprise the starting materials. In this embodiment, a center layer 202 was a substantially pure nickel (Ni) metal, while the two outer layers 204 were substantially pure aluminum (Al) metal. The three elemental layers were tack bonded together to form the composite lamina blank 205. Alternatively, multiple layers can be formed by physical vapor deposition or chemical vapor deposition of one or more metals onto a layer of another metal.

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Layers 202 and 204 were surface-prepared to remove dirt, grease and oxides, and then tack bonded. Tack bonding involved placing the layered stack of 202, 204, in a vacuum hot press and subjecting the stack to a temperature and pressure for a period of time sufficient to fix the layers to, or at least relative to, one another in a stack, while the layers remained in their substantially pure metallic state. This generally means heating to a temperature of from about 25°C to a temperature below the lowest melting temperature of the various metal layers, (in the case of Al-Ni laminae, below a temperature of about 660°C), under a pressure typically of from about 0 psi to about 30,000 psi, and more typically from about 1 psi to about 1,000 psi. A working embodiment for making a NiAl structure used a temperature of 500°C and a uniform pressure of 1,000 psi over the largest outer surfaces of the stack, in a direction orthogonal to the major surfaces of the stack, for a total of 15 minutes. The resultant composite lamina blank comprised, in this embodiment, aluminum and nickel in their substantially elemental state, though spatially fixed in relation to one another in a layered configuration.

After lamina blanks have been produced, each lamina blank, or a necessary number required for forming a given monolithic structure, is patterned as exemplified in FIG. 3. A lamina blank, comprising a set of tack-bonded layers, typically is patternable, as each of the substantially pure metal layers (or patternable intermetallic layers) is patternable. The tack-bonding process typically does not change the chemical composition of the layers, nor does it form a non-patternable intermetallic throughout that portion of the lamina blank which must be patterned. Hence, though the characteristics of each metal may be different, and therefore careful attention needs to be paid to the patterning process, the lamina blank as a unit can be patterned, being a tack-bonded composite of metal layers, at least one of which is patternable. Typically one or more of the patterned laminae will have some type of machining, such as removal of metal through machining or placement of an incision into an edge, prior to further processing.

FIG. 3 shows a lamina 302 patterned into a shape referred to as a "fin," and a lamina 304 patterned into a shape referred to as a "channel." Each of the depicted shapes was patterned by removing metal according to the specification of the final monolithic structure. For instance, in one embodiment for which the final structure serves as a heat sink, the monolithic structure

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needed a stack having one fin 302 followed by two channels 304, with that order repeated, as illustrated in FIG. 4.

Patterned laminae are stacked in the order needed to produce the geometry, topology and topography of the final monolithic structure. FIG. 5 shows one embodiment of a set of  
5 patterned laminae 502 stacked on a registration jig 504. The registration jig 504, including upright guides 506, aligns the laminae 502 with respect to one another to define the desired monolithic structure.

If the geometry of the final structure is, for instance, other than a rectangular parallel channel device, it may be desirable to register subgroups of laminae. As illustrated by FIG. 6,  
10 for example, it may be desirable to have the laminae registered in pairs 602, each pair being offset from the others within the structure. Registration jig 604 with upright guides 606 may be configured to register laminae having this arrangement, as well as other arrangements, for such a structure.

When stacked and aligned, the laminae are then all, or at least in part, rendered  
15 invariant in position with respect to one another. This can be accomplished by attaching the laminae together, or at least attaching a subset of laminae together. In one embodiment shown in FIG. 7, attaching the laminae together was accomplished by bonding using a vacuum press 702 to apply pressure of from about 0 psi to about 30,000 psi, typically about 700 psi, and generally at elevated temperatures from about 25°C to a temperature below the lowest melting  
20 temperature of the various metal layers for a limited time period, generally of from about 0.2 hour to about 1 hour, sufficient to tack-bond the laminae. In an embodiment comprising aluminum/nickel/aluminum laminae, this bonding step has been successfully accomplished at 400°C and 700 psi for 15 minutes.

Laminae can be attached by other means. For example, in another embodiment,  
25 attaching the laminae to one another was accomplished using an adhesive such as cyanoacrylate. Adhesive was applied to at least the edges of the laminae and bonding accomplished under pressure at room temperature.

An aspect of a described embodiment comprises converting a set of stacked laminae to a structure that includes an intermetallic compound. This is typically accomplished by heating  
30 the entire stack at a temperature and for a period of time sufficient to form the desired structure.

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Initially the stack is heated to a plateau temperature by raising the temperature of the stack at a rate typically in the range of from 0.1°C/minute to 100°C/minute. A typical range of plateau temperatures is from about 300°C to about the melting temperature of the intermetallic that will be formed; in the case of Ni-Al, that temperature is 1,640°C. The period of time for conversion can be in a range from about 0.25 hours to about 100 hours. Homogenous intermetallic materials can be formed, and may be preferred for particular applications. Alternatively, only a portion of two adjacent layers may form an intermetallic so that there is either a discrete metallic/intermetallic boundary, or a gradient that extends from substantially pure metal to substantially homogeneous intermetallic.

10 In one embodiment, a lamina stack comprising laminae of Al and Ni layers was heated at 1,000°C for 10 hours under reduced pressure. The result was a monolithic structure with the desired topological, topographical and geometric features. In this case, the intermetallic compound formed was NiAl.

## 15 II. Variations in Monolithic Intermetallic Structure Preparation

Processing temperatures may vary for forming particular intermetallic or metal/intermetallic materials. Temperatures are selected based on considering minimum temperatures to form an intermetallic material, such as temperatures close to, or at, the melting point of the constituent materials, or at temperatures lower than the melting point, but still resulting in intermetallic formation within a period of time reasonable for commercial applications. Such times typically are from about 0.2 hours to about 100 hours. In addition to liquid-phase bonding, solid state diffusion bonding can be employed to form an intermetallic, wherein the processing temperature is lower than the melting temperature of any of the constituent metals. Differences in the makeup of lamina blanks (number of layers per lamina, the order of metals in one lamina), also may necessitate changes in processing parameters to achieve optimal bonding, as well as optimal conversion to a monolithic intermetallic structure.

25 For intermetallics that can be shaped through machining and other patterning techniques that may include chemical as well as physical material removal at room temperature or at an elevated temperature, one or more patterned intermetallic layers may be incorporated within a set of laminae that will be processed to form a monolithic structure. Such

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incorporation of patterned intermetallic layers in a monolithic structure may be advantageous, for example, when a post is desired to provide structural support. Processing of the lamina stack may proceed via liquid-phase bonding or solid state diffusion bonding.

5 In another embodiment, a monolithic intermetallic structure may be formed starting with patternable intermetallic sheets some of which are machineable, patterning the sheets through machining and other patterning techniques, stacking and registering the patterned intermetallic sheets, and diffusion bonding the stacked and registered sheets to form a monolithic intermetallic structure. In order to ensure that the sheets will not crack as a result of the bonding pressure, the sheets are first heated to a plateau temperature for diffusion bonding, 10 and then bonding pressure is added. Since many intermetallics have high fracture toughness at elevated temperatures, pressure applied to the stacked and registered sheets after they have been raised to the diffusion bonding temperature will, in many cases, avoid crack formation in the layers.

In yet another embodiment, multi-layered laminae are patterned and then converted, 15 through application of heat and pressure, to produce a plurality of patterned intermetallic layers. The patterned intermetallic layers are then stacked and registered, and the stack is then diffusion-bonded to produce a monolithic intermetallic structure.

It may be advantageous to form a single monolithic structure from a variety of intermetallics. In order to do so, it may be necessary to form several types of lamina blanks 20 from different combinations of metals. The conversion process would then result in several different intermetallics within the same monolithic structure.

It may be advantageous to have a monolithic structure of which only a portion is intermetallic in makeup. Such a structure can be realized through appropriate choice of laminae and registration thereof.

25 It also has been found advantageous to include a lamina or layer of a pure metal positioned between two intermetallic laminae. For example, to facilitate bonding of NiAl intermetallic laminae, a substantially pure lamina of nickel has been placed between the two NiAl laminae. Working embodiments have used substantially pure lamina (e.g., commercially available nickel foil having a purity of about 99%) having a sufficient thickness to facilitate 30 bonding. While such thickness can vary, working embodiments have used pure lamina, such as

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a foil, or a deposited layer, having a thickness of from about 5  $\mu\text{m}$  to about 10  $\mu\text{m}$  thick. For this purpose, working embodiments typically have used a pure metal lamina thickness of about 7.5  $\mu\text{m}$ . The substantially pure metal layer can be deposited on the surface of the intermetallic, such as by vapor phase or bath deposition. This embodiment of applicants' disclosed method is not limited solely to use with nickel lamina or layers, and instead can be practiced with other intermetallic materials, if warranted, including without limitation those intermetallic materials specifically disclosed herein.

### III. Applications

The present invention can be used to form a myriad of devices having varying structures and topologies. Certain embodiments of such devices are described in applicants' prior patent documents, including U.S. patent application No. 09/369,679, entitled "Microlamination Method for Making Devices," and U.S. patent application No. 60/095,605, entitled "Methods for Making Devices by Component Dissociation and Microprojection Welding".

#### 1. Chemical Reactors

Monolithic intermetallic structures can be used as a chemical reactor. This embodiment typically involves placing catalysts adjacent to surfaces of the structure, such as affixing or embedding catalysts on the internal surfaces, such as apertures, patterned within. The structure formed allows fluids, including compressible fluids, to pass through a set of apertures that comprise the internal passageways of the structure. The internal surface area, when coated with catalytic material, promotes one or more chemical reactions that can occur under specific conditions, such as high temperature. Intermetallic compounds may be formed that provide good compatibility with, or possess good adherence characteristics for, the reaction catalysts needed. Intermetallics may be alloyed with catalytic metals, providing a significant benefit as a choice for a catalytic microreactor substrate. An intermetallic compound also may be selected that possesses desired heat characteristics, such as high melting temperature and low thermal conductivity, to form a chemical reactor. One such chemical reactor may have a high surface area for exposing the reactants to the catalytic material, physical characteristics such that the

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structure will not melt or deform over time, and, as a result of low thermal conductivity, not significantly reduce the temperature of the desired chemical reaction.

Other embodiments having catalysts include, but are not limited to:

5 (1) Catalytic material(s) applied to the internal or external surfaces of an intermetallic structure such as a microstructure. FIG. 8 shows a monolithic intermetallic structure 1702 which defines a fluid pathway 1704. Wall 1706 is exposed to fluid flowing through the fluid pathway 1704. Positioned adjacent to, affixed to or embedded in wall 1706 is a catalyst 1708 that may come into contact with fluids flowing through the pathway 1704.

10 (2) Catalytic material(s), held within the structure, that may come into contact with reactants passing through the structure. FIG. 9 illustrates a monolithic structure 910 that defines a fluid pathway 912. A catalyst 914 may be positioned within the fluid pathway 912, but is not affixed to nor embedded within the wall defining the fluid pathway 912. For example, the catalyst may be supported by a structure, such as a screen 916, which may be formed as part of making the monolithic structure, on which catalyst 914 rests. A fluid passing through the fluid  
15 pathway 912 can contact the catalyst 914 to promote a desired chemical reaction among the constituents of the fluid.

(3) A catalyst embedded in the surface of portions of the structure. FIG. 10 illustrates a monolithic structure, such as an intermetallic structure 1010, that defines a fluid pathway 1012, the side walls of which have been embedded with catalytic material that extends beneath the  
20 surface of the fluid pathway 1012. Should the catalyst become eroded due to exposure to continued contact with the reactants flowing through the structure, this arrangement maintains the presence of the catalyst in the reaction path for a prolonged period of time.

Various catalytic materials may be used including, without limitation: inorganic catalysts, such as finely divided metals, e.g., platinum and palladium, and carbon; organic  
25 catalysts, including biological materials, such as nucleic acids, DNA, RNA, enzymatic materials; and combinations thereof.

Other methods for including catalytic material into the monolithic intermetallic structure are also within the scope of this disclosure.

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## 2. Materials with Special Properties

Monolithic intermetallic structures can be made by selecting materials based on magnetic properties, such as magnetic susceptibility. Still other applications may take advantage of other properties of intermetallics, for example, but not limited to, electrical conductivity, superconducting transition temperature, heat capacity, thermal conductivity, chemical reactivity, and are included within the scope of this application.

## 3. Microchannel Arrays

Microchannel arrays made using the disclosed fabrication process provide a number of advantages in addition to size including, for example, high surface-area-to-volume ratio for substances passing through the structure. The additional surface area is provided by the internal passageways defined by the topology and geometric configuration of the monolithic structure. Microchannel arrays are particularly useful for making portable devices, such as portable microchemical reactors, portable fuel cells, portable air purification systems for use where the air is highly contaminated with noxious substances, high temperature heat exchangers, and other miniaturization applications.

Macroscopic devices also can be formed where a very high surface area-to-volume ratio is desired. In the latter case, a bank of microchannel array structures can serve a macroscopic application.

## 4. Macrochannel arrays

Macroscopic devices using a large-scale, monolithic, intermetallic structure may be preferable to microchannel arrays. For example, a macroscopic device may be preferable in a large-scale, heat-recovery application, e.g., exhaust heat stack, where a large cross-sectional area must be traversed, and where performance of the device utilizing the structure is not significantly improved through a very high internal surface area-to-volume ratio. Fabricating macroscopic, large-scale, monolithic, intermetallic structures uses the same general fabrication methodology disclosed herein, with the possible need for modifications to accommodate increased size, such as to avoid deformation of the internal geometries due to material sag during fabrication.



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Material sag may be prevented by using features such as posts, which support long spans of laminae. These techniques also may be applicable to smaller geometries such as microreactors and meso-scale devices.

FIGS. 11A and 11B show a stack of patterned laminae, with a lamina 1102 comprising three metal layers. In between alternate laminae are one or more posts 1104, that provide structural support, and also transmit pressure between laminae. A post can be formed as a feature machined into a lamina, i.e., blind machined feature as in FIG. 11A. Alternatively, the illustrated posts 1104 can be made starting from a lamina and machining away the excess to form a post 1104 as in FIG. 11A, the lamina comprising a sandwich made up of a plurality of metals, or posts 1104 in FIG. 11B can be made from a machineable intermetallic material. FIG. 12 illustrates the stack after conversion to a monolithic intermetallic structure 1202, with posts 1204.

#### IV. Topological/Geometrical Variations

The disclosed embodiments can be generalized to other topologies and geometries, which may be preferable for specific applications. For example, FIG. 13 illustrates using concentrically, or substantially concentrically, registered cylindrical laminae 1302. Laminae 1302 comprising an aluminum-nickel-aluminum sandwich can be heated to a temperature of from about 300°C to about 1,640°C, to form a homogeneous, or substantially homogeneous intermetallic, a discrete intermetallic/metal boundary, or a gradient from one substantially homogeneous metal through an intermetallic to another substantially pure homogeneous metal.

FIG. 14 illustrates a device having a variable cross-sectional area 1402 within the internal geometry. The design illustrated by FIG. 14 creates regions of high fluid velocity.

FIG. 15 illustrates a well 1504 within a structure 1502 that serves as a reservoir for a fluid, particularly a liquid reactant. The reactant is allowed to come into contact with fluids passing through a fluid pathway 1506 within the structure 1502.

FIG. 16 illustrates a monolithic intermetallic structure 1602 having a main input 1604 and auxiliary inputs 1606 for injection of a reactant at a particular point in the primary substance's path through the structure. Structure 1602 also includes a main output 1608, auxiliary outputs 1610, and exhaust ducts 1612, to enable, for instance, pressure reduction at a

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particular point in the substance's path. Other geometries and topologies may be considered, and fall within the scope of this disclosure.

Structures may be fabricated that comprise substructures, some of which may be intended to be freely moveable within the structure after fabrication. The substructures are  
5 coupled during fabrication to internal members and other substructures by fixture bridges, which are removed after fabrication of the intermetallic is complete. Fixture bridges, and the use thereof, are described in U.S. patent application No. 09/369,679, entitled "Microlamination Method for Making Devices," which is incorporated herein by reference. For such structures intermetallics may be advantageous, due to their physical properties, such as low thermal  
10 conductivity and high melting temperature.

## V. Examples

The following examples are provided to illustrate certain features of the present invention. The scope of the invention should not be limited to those features exemplified.  
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### Example 1

This example concerns designing and using a fixture for registering plural lamina by TEER. Stiffness is believed to be an important factor in determining whether stacked laminae are registered or buckled by the registration force applied during TEER. As a result, two  
20 factors, laminae thickness and device length, were varied. Two device sizes, 12.7 millimeters and 25.4 millimeters, and two laminae thicknesses 50.8 microns and 76.2 microns, were used. Microlamination was used to produce a test article 1700, as shown in FIGs. 17a and 17b. Test laminae 1702, 1704, 1706 were patterned from 304 stainless steel shim stock by laser ablation at the 4<sup>th</sup> harmonic of an Nd:YAG laser (266 nm). Five windows 1708 were patterned on the  
25 laminae 1702 so that the alignment of the laminae could be determined visually. After patterning, the laminae 1702, 1704, 1706 were washed with acetone, ethanol and deionized water. The laminae 1702, 1704, 1706 also were cleaned in an ultrasonic cleaner using Citranox for about 20 minutes. The laminae 1702, 1704, 1706 were then rinsed again with acetone, alcohol and deionized water.

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The washed laminae 1702, 1704, 1706 were then positioned on a registration fixture 1800 as schematically illustrated in FIG. 18. The laminae 1702, 1704, 1706 were diffusion bonded in a vacuum hot press at 900°C at 6.55Mpa (950 psi) for two hours. The vacuum chamber was heated to the 900°C bonding temperature before the bonding pressure was applied. This allowed the laminae edges to properly register before bonding. The bonding pressure was relieved before cooling so that the laminate could contract uniformly without any induced stress.

Layer-to-layer misalignment was measured and viewed on screen using a LEICA DML microscope coupled to a charge-coupled device (CCD) camera. The laminate was placed on the stage of the microscope and focused until the registration marks 1710, 1712 were clearly seen at 200X with a resolution of 0.3-0.4 microns. Line markers 1712 patterned on lamina 1704 could be seen through window 1708 etched in top lamina 1702 placed over a lamina 1704. The misalignment defined by the markers 1712 on the lamina 1704 relative to the marker on the lamina 1702 was measured optically. Misalignments for all positions viewable by the windows 1708 were then determined, resulting in eighty total measurements. Twenty of the eighty measurements were verified using SEM, and no statistically significant difference was seen between the two measurement methods.

An overall misalignment for the eighty measurements taken was 4.3 microns. The accepted misalignment standard is about 50 microns. Madou, "Fundamentals of Microfabrication" (1997). The averages for the tested combinations are provided below in Table 2, which shows misalignment errors achieved for different lamina thicknesses and channel spans.

Lamina Thickness		
Device Length	50.8 $\mu\text{m}$	76.2 $\mu\text{m}$
12.7 mm	3.96 $\mu\text{m}$	2.03 $\mu\text{m}$
25.4 mm	8.08 $\mu\text{m}$	3.14 $\mu\text{m}$

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Table 2 shows that two variables may be important in determining alignment precision, laminae thickness and device length. For thickness, the thicker the lamina, the better the alignment. Compare the misalignments for 76.2 microns thick lamina to 50.8 microns thick lamina. Also, shorter laminae have reduced misalignment, as can be seen by comparing the results for lamina  
5 having a length of 12.7 mm and lamina having a length of 25.4 mm.

### Example 2

Surprisingly, it has been found that the precision obtained using TEER is better than that predicted when considering the precision of the fixture. For example, a graphite fixture  
10 (schematically illustrated by FIG. 18) was used for this example. The fixture was milled on a milling machine having a resolution of about 12.7  $\mu\text{m}$ . However, the results presented in Table 1 show that precisions of less than about 5  $\mu\text{m}$  are possible when using this fixture to practice TEER. In other words, registration with misalignments of less than about 10 microns, and typically less than 5 microns, are possible using a fixture having tolerances in the 10s of  
15 microns.

This observation was tested by making devices of different lengths and registering the laminae necessary to make such devices using a fixture with a fixed length. FIG. 19 shows the results. The misalignment experienced remains constant over the interval of interference between the laminae and the fixture. The length of this interval is over 100  $\mu\text{m}$ , which well  
20 exceeds the machine tool tolerance. The TEER process therefore can accommodate lower tolerances in the fixture relative to that desirable in the assembled monolithic device.

### Example 3

This example describes the synthesis of nickel aluminide foils. The starting materials  
25 used in this experiment were commercially pure aluminum (99% Al), and nickel foils (99% Ni). Required thicknesses of the starting materials were calculated to provide a 1:1 atomic ratio of Ni to Al (stoichiometric NiAl). Ni has an atomic mass of 58.71 g/mol and a density of 8.90 g/cm<sup>3</sup>; therefore, a cubic centimeter of Ni contains 0.1516 mole of Ni. With an atomic mass of 26.98 g/mol and a density of 2.70 g/cm<sup>3</sup>, a cubic centimeter of Al is 0.1001 moles of Al atoms.

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Therefore, with an equal surface area, a thickness ratio of Al to Ni of 3:2 provides a stoichiometric NiAl phase.

Two sequences of elemental foils were intentionally investigated for nickel aluminide foil synthesis. The first sequence was Al-Ni-Al-Ni-Al and the second sequence was Al-Ni-Al.  
5 The Al-Ni-Al-Ni-Al structure has been found to be inferior due to void formation in the foil.

Foils with the required thicknesses were sheared into blanks and cleaned in an acid detergent. To make an individual composite foil, Al and Ni foils with a specified thickness were stacked in a sequence, either Al-Ni-Al-Ni-Al or Al-Ni-Al. Stacks of elemental foils were then tack bonded by diffusion bonding to provide an intimate contact between the Ni and Al  
10 foils. In this experiment three different nominal thicknesses of the composite foils were obtained: 63.5  $\mu\text{m}$ , 127  $\mu\text{m}$ , and 254  $\mu\text{m}$ . A graphite fixture was used in the tack bonding step. Each individual stack was separated from each other by a graphite plate to prevent bonding to each other. The tack bonding conditions for these elemental foils were at 500 °C, 3.9 MPa, and a 15-minute holding time. This tack bonding process was done in a vacuum environment of  
15 about 0.01 Pa. After tack bonding, each stack of elemental foils transformed into a composite foil of the accumulated thickness. Unbonded areas, typically at the edges, were trimmed.

The composite foils were heat treated at various conditions. The melting point of aluminum is about 660 °C. Therefore, to study the formation of NiAl in both solid and liquid state of aluminum, annealing temperatures were intentionally selected both below and above  
20 660 °C. Selected annealing temperatures were 600 °C, 650 °C, 670 °C, 800 °C, and 1000 °C, and the annealing times were chosen to bridge the reaction times at 2, 4, 8, and 15 hours. Annealing temperatures of 650 °C and 670 °C were purposely selected close to the melting point of aluminum to observe any abrupt change in the formation of NiAl when the system changed from solid-solid to solid-liquid reactions. With combinations of these annealing temperatures  
25 and times, 20 annealing conditions were used to treat the composite foil with each thickness, and two replicates were performed for each treatment.

A graphite fixture was used in this annealing process. Graphite plates were used to separate each composite foil from each other, and to provide a slight pressure on the foils. This heat treatment process was operated under a vacuum of about 0.01 Pa.

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The annealed foils were sectioned perpendicular to the foil interfaces and then molded in epoxy resin before polishing. Formations and depletions of intermetallic phases in the foils were studied. The phases presented in the foils were first identified using wavelength dispersive spectroscopy (WDS) to investigate their nickel and aluminum contents.

- 5 Concentrations of both elements were measured at 1  $\mu\text{m}$  interval. The already-identified phases were then studied under an optical microscope. The foils also were etched to reveal their microstructures, especially the grain size. The solution that was used to reveal the foils microstructures was a mixture of  $\text{FeCl}_3$ ,  $\text{HNO}_3$ , and methanol in the ratio of 5 grams to 2 ml to 99 ml, respectively. Lastly, flatness and surface roughness of the homogeneous NiAl foils were  
10 investigated using a surface profiler. Scan length was 20,000  $\mu\text{m}$ , which was the maximum capability of the machine.

After tack bonding elemental foils at 500 °C for 15 minutes with 3.9 MPa applied pressure, no void was present at the interfaces. A thin layer of intermediate phase was observed between Ni and Al foils.

- 15 The stacking order of the elemental foils is an important consideration for producing intermetallic foils from elemental foils because Kirkendall porosities play an important role in diffusion of dissimilar materials. During the synthesis of nickel aluminide foil from composite foil of Al-Ni-Al-Ni-Al structure, significant porosities due to the Kirkendall effect were found. The foil was annealed at 1,000 °C for 3 hours.

- 20 The composite foil was separated into two halves by a plane of porosities after 3 hours of annealing at 1,000 °C. These porosities are the Kirkendall porosities. In this system, aluminum atoms move into another species (Ni atoms) at a higher rate than the counterpart atoms. The vacancies that are left behind by the aluminum atoms are filled by the moving nickel atoms, but at a slower rate. Thus, these vacancies accumulate throughout the aluminum  
25 foil as the diffusion process progresses. Finally a plane of voids is formed and separates the composite foil of Al-Ni-Al-Ni-Al into two halves. This void formation prevents the success of nickel aluminide foil synthesis from the Al-Ni-Al-Ni-Al composite foil.

- Annealed foil shape change was significant if not restrained. The composite foil was curled after annealing if it was not sandwiched by platens. This might result from phase  
30 transformations from elemental nickel and aluminum to nickel aluminide during the heat

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treatment. Since both elemental Ni and Al have fcc structures, but NiAl has a CsCl structure, the elemental atoms have to rearrange themselves, and this might cause a foil shape change during heat treatment. Thus, to make a flat nickel aluminide foil, slight pressure or a proper stretching method was applied on the foil during the heat treatment. Annealed foils that were

5 heat treated at 1000 °C for 10 hours without sandwiching by platens showed severe macroscopic shape changes. In the synthesis of nickel aluminide foil from elemental nickel and aluminum foils, volumetric contraction of the foil during the heat treatment was observed. This is due to phase transformation from Ni and Al elements to NiAl compound. In making a NiAl foil from

10 elemental Ni and Al foils, the volumetric ratio of Ni and Al is 40 and 60% of the volume of composite foil, respectively. The volume of NiAl foil is 88.40% of that of the starting composite foil. In other words, there is an 11.60% volumetric contraction during the transformation from the composite foil to NiAl foil. Thus, fully developed nickel aluminide foils are preferable in place of the composite Ni-Al-Ni foils as the starting material in building

15 homogeneous nickel aluminide foils provides better dimensional accuracy than those fabricated from the composite foils.

#### Example 4

A NiAl intermetallic monolithic structure has been fabricated from Al and Ni starting

20 materials. Lamina blanks were formed as in FIG. 2, using substantially pure Al foil (25.4 x 10<sup>-6</sup> m. thick) and substantially pure Ni foil (50.8 x 10<sup>-6</sup> m. thick). The metal foils were cut into square layers of side 7.5 x 10<sup>-2</sup> m.

The metals were surface-prepared. Specifically, each of the layers was cleaned with acetone. The Ni was then etched in a solution of 20% by volume HCl and 80% by volume

25 distilled water. The Al was etched with a solution consisting of 50% by volume HNO<sub>3</sub> and 50% by volume distilled water. Both metals were agitated in their respective etching solutions for approximately 5 minutes.

A lamina blank comprising one Ni layer sandwiched on either side by an Al layer was produced by low-temperature tack bonding in a vacuum hot press at 500°C and 1,000 psi for 15

30 minutes, at 10<sup>-4</sup> torr pressure. Each lamina blank was patterned via laser ablation with an ESI

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4420 Laser Micromachining System with a Q-switched 532 nm Nd:YAG laser rail. Patterned laminae formed included both fins 302 and channels 304, as in FIG. 3.

Patterned laminae were stacked according to the scheme shown in FIG. 4. Registration was accomplished using a fixture with three molybdenum fixturing pins that were used to locate the edges of the laminae, and a base made of graphite. The laminae were tack bonded adhesively with cyanoacrylate at room temperature, under an exerted pressure of 700 psi. Conversion of the laminae to an intermetallic compound was achieved by heat treating the tack-bonded stack in a vacuum oven. Laminae were synthesized and aggregated by self-propagating, high-temperature synthesis (SHS) and subsequent heat treatment to homogenize the microstructure of each lamina in tandem with diffusion bonding the laminae collectively in a vacuum hot press at elevated temperature and pressure. The stack was positioned between two platens with minimal pressure (under 100 psi), and heated at a rate of 10°C per minute to a temperature of 1,000°C. The sample was then held at this temperature for 10 hours, resulting in the desired monolithic intermetallic structure.

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#### Example 5

An NiAl intermetallic monolithic structure is fabricated from Al and Ni starting materials. Lamina blanks are formed as in FIG. 2, using substantially pure Al foil and substantially pure Ni foil. The metals are surface-prepared.

20 A lamina blank comprising one Ni layer sandwiched on either side by an Al layer is produced by low-temperature tack bonding in a vacuum hot press at 500°C and 1,000 psi for 15 minutes, at  $10^{-4}$  torr pressure. Positioning an Ni layer between two adjacent Al layers ameliorates problems associated with Kirkendall porosities that arise with the Al foil. Some laminae blanks are patterned. Conversion of the laminae to an intermetallic compound is achieved by heat treating each of the tack-bonded laminae in a vacuum oven. Laminae were synthesized and aggregated by self-propagating high-temperature synthesis (SHS) and subsequent heat treatment to homogenize the microstructure of each lamina in tandem with diffusion bonding the laminae collectively in a vacuum hot press at elevated temperature and pressure. The laminae are heated at a rate of 10°C per minute to a temperature of 1,000°C. The sample is then held at this temperature for 10 hours, resulting in the intermetallic NiAl.

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Patterned and unpatterned intermetallic laminae are stacked. Registration is accomplished using a fixture. The laminae are tack bonded adhesively with cyanoacrylate at room temperature, under an exerted pressure of 700 psi. Conversion of the laminae to a monolithic intermetallic structure is achieved by diffusion bonding through heat treating the tack-bonded stack in a vacuum oven. The stack is positioned between two platens with minimal pressure (under 100 psi), and heated at a rate of 10°C per minute to a temperature of between 1,700°C and 1,100°C. The sample is then held at this temperature for between 1 and 24 hours, resulting in the desired monolithic intermetallic structure.

10

**Example 6**

Starting with intermetallic laminae, some laminae are patterned, through machining and other patterning techniques. For instance, the intermetallic compounds NiAl and Ni<sub>3</sub>Al can both be machined via chemical etching using a solution of H<sub>2</sub>O (25 mL), HCl (50 mL), FeCl<sub>2</sub> (15 grams), and CuNO<sub>3</sub> (3 grams); the intermetallic compounds FeAl and Fe<sub>3</sub>Al both can be machined using chemical etching and a solution comprising 6 parts H<sub>3</sub>CCO<sub>2</sub>H, 4 parts HNO<sub>3</sub>, and 2 parts HCl. Patterned and unpatterned intermetallic laminae are stacked and registered. Registration is accomplished using a fixture. The laminae are tack bonded adhesively with cyanoacrylate at room temperature at 700 psi. Conversion of the laminae to a monolithic intermetallic structure is achieved by diffusion bonding through heat treating the tack-bonded stack in a vacuum oven. The stack is positioned between two platens with minimal pressure (under 100 psi), and heated at a rate of 10°C per minute to a temperature of between 1,100°C and 1,700°C. The sample is then held at this temperature for between 1 and 24 hours, resulting in the desired monolithic intermetallic structure.

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**Example 7**

According to the method of Demura *et al.*, rods of boron-free binary stoichiometric Ni<sub>3</sub>Al can be grown by the FZ method at a growth rate of 25 mm/hour. The crystal diameter is kept constant during the crystal growth to obtain high single crystallinity by controlling the lamp power. The grown rods can be sectioned into sheets along the growth direction by electric discharge machining. Sheets having a thickness of from about 1 to about 2 millimeters can be

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cold rolled to about 300  $\mu\text{m}$  in thickness using four-high mills with a work roll diameter of 110 millimeters. The sheets can be rolled a second time using cemented carbide rolls having a roll diameter of about 75 millimeters.

The above process was used to make foils. These foils were then patterned using a  
5 YAG:Nd laser. A crossover fluid flow laminate was then made by registering the patterned  $\text{Ni}_3\text{Al}$  foils, registering the patterned foils by TEER, and converting the registered foils to a monolithic structure by applying heat and pressure to the stack.

#### Example 8

10 FIG. 20 illustrates  $\text{Ni}_3\text{Al}$  laminae used in a microlamination procedure to form a  $\text{Ni}_3\text{Al}$  intermetallic microchannel geometry 2000. The procedure involved laminae patterning, laminae registration, and diffusion bonding of the laminae to produce a monolithic structure. The laminae were formed using 85  $\mu\text{m}$  thick  $\text{Ni}_3\text{Al}$  foil acquired from Dr. Toshiyuki Hirano at the National Research Institute for Metals (NIMR) Japan. An ESI 4420 Laser Micromachining  
15 System with a 266 nm UV laser rail was used to produce a patterned lamina from the blank. Specifically, as illustrated by FIG. 20, the patterned laminae used to assemble the device included spacer 2002, end plate 2004, channel laminae 2006, 2008, fin lamina 2010, channel laminae 2012, 2014, fin lamina 2016, and spacer lamina 2018. The laminae 2002-2018 were TEER registered using a fixture having alignment pins to constrain the stack of laminae at the  
20 edges. Laminae 2002-2018 were diffusion bonded by heat treating the stack in a vacuum hot press at elevated temperature and pressure. The laminae 2002-2018 were positioned between two graphite platens applying 900 psi pressure and heated at a rate of 10°C per minute to a temperature of 900°C. The laminae were held at this temperature for 40 hours to form the monolithic device. The device was leak tested under more than 1 atmosphere of air pressure  
25 under water. No leakage between the channels as well as along the edges of the device was observed.

#### Example 9

This example concerns plating aluminum with electroless nickel after treating the  
30 aluminum foils with a Zincate process to remove  $\text{Al}_2\text{O}_3$ , thereby improving the bonding of  $\text{NiAl}$

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laminae. Electroless nickel plating was preferred to the conventional electroplating for its simple setup, ease of use and uniform deposition over the surface.

Aluminum forms an oxide layer when exposed to air. This presents a problem when plating aluminum, as the oxide layer prevents the plating solution from sticking to the surface.

5 By using the Zincate process as a preplate dip, any oxide layer present may be chemically removed and at the same time a layer of zinc is applied onto the surface of aluminum foil. Zinc protects the aluminum until it is ready to be plated. As the part is lowered into the plating tank, the zinc is etched away by the nickel solution and plating proceeds onto a chemically clean surface.

10 Aluminum laminae were cut into 2.54 cm x 2.54 cm blanks out of 50.8  $\mu$ m thick commercially pure aluminum foil. The blanks were cleaned using acetone then acid-etched with a 50% by volume solution of  $\text{HNO}_3$  to remove native oxides. Single Zincate and double Zincate processes are known for preparing aluminum surface prior to electroless nickel plating. The following steps were followed for the double Zincate process: (1) Non-etch soak clean; (2) 15 rinse; (3) acid etch; (4) rinse; (5) desmut in nitric acid, 50%; (6) rinse; (7) Zincate - long immersion; (8) rinse; (9) strip in 50% nitric acid; (10) rinse; (11) Zincate - short immersion; (12) rinse; and (13) electroless nickel plate.

After following steps 1 to 6 for cleaning the aluminum surface, a 25% by volume Zincate solution, purchased from Caswell Inc., Palmyra, New York, was made. Specifically, 20 ml of Zincate were poured into a Pyrex beaker, which subsequently was filled to the 200 ml mark with distilled water. The solution was heated to 75°F (~29°C) on a hot plate. On acquiring the required temperature aluminum laminae were completely immersed into the Zincate solution for 2 minutes. A uniform gray appearance is usually a sign of a properly Zincated surface. Laminae were taken out of the solution and steps 8 to 10 were followed. 25 Laminae were again immersed into the Zincate solution for 15 seconds, followed by steps 12 and 13.

Electroless nickel plating system was purchased from Caswell Inc. The system consists of 2 main ingredients, parts A and B. Parts A and B are mixed with distilled water to make the nickel plating solution. In order to make the solution, 25 ml of part A were mixed with 75 ml of 30 part B in a Pyrex beaker. The beaker was then filled to the 500 ml mark with distilled water.

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The Pyrex beaker was put on a hot plate having a built in agitator, and heated to 195°F (~91°C). After the solution acquired the desired temperature, aluminum laminae preplated with Zincate were deposited at the bottom of the container. During the plating procedure the container was constantly agitated with the built in agitator. The deposition rate for electroless nickel plating is about 25  $\mu\text{m}$  per hour. Calculations for the required deposition of nickel on 50.8  $\mu\text{m}$  aluminum to have 50 atomic % of nickel and aluminum were carried out. In order to have 50 atomic % of nickel and aluminum to form NiAl, a 33.65  $\mu\text{m}$  thick deposition of nickel is required on 50.8  $\mu\text{m}$  thick aluminum laminae. Both one-sided and two-sided plating methods were used. For one-sided plating, one side of every aluminum lamina was covered with pressure sensitive adhesive (PSA) tape. For one-sided plating, aluminum laminae were immersed in the nickel plating solution for about 92 minutes. For two-sided plating, laminae were immersed in the solution for about 45 minutes.

The electroless-nickel-plated aluminum laminae were rinsed with deionized water and dried. The laminae were placed in a graphite fixture having three tungsten pins for edge alignment. The inside surface of the fixture was lightly coated with magnesium hydroxide, to prevent the laminae from sticking to the fixture. The fixture was placed in a vacuum hot press with minimal pressure on the fixture (the hydraulic pump of the press was turned off). The pressure in the press was reduced to  $10^{-4}$  torr. The laminae were converted to an intermetallic compound by heat treating the stack at a rate of 10°C per minute to a temperature of 1,000°C. The sample was held at this temperature for 10 hours.

Zincating of aluminum laminae was accomplished successfully. In the case of two-sided Zincating a uniform gray appearance was observed on both sides of the laminae. For one-sided Zincating the Zincate solution impinged under the taped side along the edges.

Several unsuccessful attempts were made to counteract this problem with different tapes as well as photoresist deposition. The photoresist did not stand to the Zincate solution and was gradually dissolved. Also nitric acid was used as a Zincate stripper to remove the unwanted Zincate, but it somehow stripped the Zincate on the other side as well. Therefore, two-sided Zincating was preferred. After successful Zincating, laminae were obtained in 45 minutes. The surface was devoid of any puts or cracks, and the quality of adhesion to the laminae was good. Tape test was conducted to check the nickel adhesion to the surface.

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A 609.6  $\mu\text{m}$  thick stack of nickel plated aluminum was bonded in the vacuum hot press. Part of the converted laminae bonded with the tungsten pins, indicating that the molten aluminum flowed. Total thickness of the stack was reduced to 508  $\mu\text{m}$ .

Different types of baths have been developed for electroless nickel plating e.g., nickel-phosphorus bath, further categorized into acid nickel-phosphorus and alkaline nickel-phosphorus baths, and nickel boron baths, etc. An acid nickel-phosphorus bath with a phosphorus content of 7% was employed in this example. The melting temperature of electroless nickel deposits vary widely, depending upon the amount of phosphorus alloyed in the deposit. A generally accepted melting point is about 1,616°F (880°C) for deposits from processes with approximately 7 to 9% phosphorus. This temperature corresponds to the melting point of nickel phosphide ( $\text{NiP}_3$ ), which precipitates during heating of electroless nickel deposits. The melting of  $\text{NiP}_3$  caused the nickel deposition to flow resulting in a loss of shape of the laminae. Another reason for the material flow was absence of the oxide layer on the aluminum laminae, as it was completely removed via the Zincate process. This reemphasized the desirability of  $\text{Al}_2\text{O}_3$  to hold liquid aluminum in place at high temperature.

### Example 10

This example considers the effects of temperature, pressure, time and metal or alloy composition on the production of articles, and particularly considers the effects of these parameters on fin warping in a microchannel array.

Reactive diffusion bonding was employed as a joining technique in this example. Commercially pure (99.99%) Ni foil was used as the filler metal. Two types of foils were used to investigate the effect of foil compositions on foil warpage due to bonding. The first foil type was a composite of an intermetallic compound ( $\text{Ni}_2\text{Al}_3$ ) and pure nickel. A homogeneous NiAl foil was used as a second starting material. To prepare the composite foil, elemental Ni and Al foils were tack bonded at 500 °C, 575 psi, for 15 minutes, and then heat treated at 600 °C for 2 hours. Chemical composition analysis of the foils indicated the desired chemical compositions were achieved.

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Foils of a particular thickness can be selected to provide both the final thickness of the lamina and the correct stoichiometric relationship of the constituent elements in the desired lamina. For this example, both types of foils had a nominal thickness of 127  $\mu\text{m}$ .

The blank foils of both types were then patterned using 532-nm laser micromachining. Cracking, due to the machining technique, was not observed during this stage. A pure Ni foil was inserted between the laminae as filler metal to promote laminae bonding.

A test article was intentionally designed as a bridge to emulate the fin of a microchannel device. Geometry and cross section of the patterned foils and filler metal are shown in Fig. 21. The dimensions of the bridge structure are 5080  $\mu\text{m}$  wide and 10,160  $\mu\text{m}$  long.

After the patterning step, the foils and filler metals were cleaned sequentially using acetone, methanol, and de-ionized water to remove grease and other contaminants from the laminae surfaces. These contaminants can hinder diffusion bonding of the materials. The laminae were then registered in the designed sequence. A graphite fixture with edge alignment was employed to register all specimens during bonding.

The foils were diffusion bonded at various conditions in a vacuum environment to study stability of the bridge structure and diffusion bonding of the foils. For every bonding cycle, the specimens were heated from and cooled down to room temperature. Deflection of the bridge structure was measured by a profiler. The profiler's stylus was traced along the length of the bridge to obtain magnitude of the warpage. The specimens were then cross-sectioned to observe bond quality at the bond interfaces.

Since this example requires severe conditions to bond the specimens, the number of trials was reduced using a fraction factorial designed experiment. Process parameters investigated in this study were bonding temperature, pressure, time, and type of foil. Each parameter was run at two levels. A  $3 \times 2^{4-1}$  fractional factorial design was created to study bonding parameter effects on warpage of nickel aluminide foils in reactive diffusion bonding. 24 runs were required for this fractional factorial design while 48 trials ( $3 \times 2^4$ ) are required if the full factorial design was selected.

The experimental conditions for the selected fractional factorial design are shown in the top part of Table 3 provided below. The "Low" and "High" pressure was set at 1,500 and 3,000

psi, respectively. Since the set pressures decreased from the set points during the example, the actual values were recorded when the pressures reached constant levels. It is assumed that before bonding, all specimens for each type of foil are identical. The example trials were run in a random order to average out the effects of confounding factors that may be present.

5

Temperature (°C)	Time (Hours)	Pressure	Foil Composition
1. 600	2	Low	Composite
2. 600	8	Low	Homo
3. 800	2	Low	Homo
4. 800	8	Low	Composite
5. 600	2	High	Homo
6. 600	8	High	Composite
7. 800	2	High	Composite
8. 800	8	High	Homo
9. 800	8	Low	Home
10. 800	8	High	Composite
11. 600	8	Low	Composite
12. 800	2	High	Home
13. 800	2	Low	Composite
14. 600	2	High	Composite
15. 600	8	High	Homo
16. 600	2	Low	Homo

Table 3

Since it is typical for fractional factorial designs that some effects are confounded with one another, a second set of trials (trials 9-16) was designed to separate the confounding of these effects. The number of trials in this phase was 8 runs without replication. Therefore, the total number of experiments in this investigation was 32 (24 + 8) runs.

10

Bonding time and temperature had significant effect on fin warpage ( $p$ -value  $< 0.05$ ). Fin warpage increased with increased bonding time and bonding temperature. Actual bonding pressure also appeared to significantly effect warpage ( $0.05 < p$ -value  $< 0.10$ ).

5 An important conclusion from this example is that foil composition does not affect the warpage. This means that in the foil synthesis stage, it is not necessary to heat treat the composite foil until a fully homogenized foil is produced, e.g., homogeneous NiAl. Homogenization can be done during the subsequent bonding process. Hence, production time of the intermetallic microchannel devices will be reduced by decreasing heat treatment time.

10 The widely used testing method to access the bond quality of diffusion-bonded specimens is the tensile test on the bonded samples (Pilling *et al.*, 1984; Ridley *et al.*, 1992; Partridge and Wisbey, 1995). However, due to brittleness of the experimental samples, this testing method was not viable to assess bond quality. Optical observation was instead performed to evaluate the bond quality.

15 For the composite foils, bonding conditions of 800 °C, 1,500 psi for 8 hours showed a good bond quality. There was no interfacial void left between the base metal and filler metal. The filler metal fully reacted with composite foils. Under a light microscope, the compound formed from the reaction showed orange color. This orange compound was the intermediate phase between the  $\text{Ni}_3\text{Al}$  and NiAl phase. If the compound is annealed longer, it transforms to the NiAl phase. However, the average fin warpage due to these bonding conditions was  
20 relatively large (30.36  $\mu\text{m}$ ).

For NiAl foil bonding, the combination of a bonding temperature of 800 °C, a pressure of 3,000 psi, and a holding time of 8 hours provided a good bond between the laminae and the filler metals. Under an optical microscope, the reaction between the foil and filler metal formed two layers of chemical compounds. The inner layer was  $\text{Ni}_3\text{Al}$  intermetallic, and the outer  
25 layers were the intermediate phase between the  $\text{Ni}_3\text{Al}$  and NiAl phase. Although the bond quality was good and could provide a leak tight device, the average fin warpage due to these bonding conditions was 52.27  $\mu\text{m}$ . When the bonding conditions were changed to 600 °C, 1,500 psi for 8 hours, no reaction between the foil and filler metal was observed although a small magnitude of fin warpage (15.33  $\mu\text{m}$ ) was achieved.



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This example shows that bonding time and temperature have significant effects on fin warpage. The fin warpage increased with increased bonding time and bonding temperature, and it was suggestive, but inconclusive, that the actual bonding pressure also had a significant effect on fin warpage. It is desirable to simultaneously optimize minimize fin warpage and maximize bond quality, especially at high volume production since an optimized bonding process could increase productivity and decrease production cost. Simultaneous optimization of multiple responses might be achieved by several approaches, such as using overlaying contour plots, a mathematical search algorithm, or a heuristic optimization procedure (Derringer and Suich, 1980; Myers and Montgomery, 1995; Back, 1996; Ansari and Hou, 1997; Langner *et al.*, 2000).

#### Example 11

This example describes a high volume process for producing iron aluminide microchannel arrays. Iron aluminide foils have been synthesized from powder with retained ductility. These foils can be patterned, bonded and normalized using the economical methods stated below.

The ductile aluminide foil is patterned by a machining or other forming technique, such as laser machining or blanking. The patterned foils are then stacked, registered in a graphite fixture and diffusion bonded to build microchannel arrays. Heat treatment can be performed in a system comprising a furnace and a conveyor through the furnace. The arrays are conveyed through the furnace at a rate selected to provide the appropriate furnace residence time. Heat treatment may be needed in tandem with diffusion bonding to normalize the composition or control the microstructure (e.g. produce large grain size to resist creep) of the foil. Additional heat treatment may be needed after diffusion bonding to complete the normalization or grow larger grains within the foil. This can be achieved by adding heat treatment time to the end of the diffusion bonding cycle without removing the material from the furnace, including increasing the residence time in a conveyORIZED furnace.

#### Example 12

This example concerns high-volume fabrication procedures of NiAl intermetallic microchannel arrays. High volume products methods are required as production volumes

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expected for micro gas turbine recuperators are estimated to be 1,000 – 10,000 per year or 4 to 40 per day.

High purity aluminum (Al) and nickel (Ni) foils were obtained commercially. The thicknesses of the starting materials were selected to provide the atomic ratio 1:1 nitrogen to aluminum (thickness ratio of Ni to Al is 2:3). The elemental foils are heat-treated to make NiAl blanks. A slight positive pressure is applied to the foil during conversion to prevent warpage due to phase transformation. This pressure can be applied by the weight of plates, such as graphite plates, in an inert gas furnace or by a hot isostatic press. The pressures is a nominal pressure, such as less than about 50 psi, more typically less than 10 psi, and even more typically about 1 psi or less. Working embodiments have used pressure plates weighing about 200 grams with a surface area of about 1.5 inches by 1.5 inches, which corresponds to an applied pressure of about 0.2 psi.

The material used to make the plates or press platens can react with the elemental materials selected, or the intermetallic material produced from the elemental materials, under the conditions used to produce the intermetallic or a monolithic device. The composition of the plates therefore can be selected to minimize such reactivity, and hence contamination, of products produced using the method. For example, substantially inert materials, such as  $\text{Si}_3\text{N}_4$ , can be used as the material from which plates are made. Materials selected to provide advantageous results also can be selected. For example,  $\text{TiB}_2$  is known to be good strength enhancing agent for certain alloys, such as the titanium alloys. Thus, plates made from this material can be used to affirmatively change the properties of materials used to make devices as discussed herein. The plates also can be made from other materials, if economically and chemically feasible to do so.

Heat treatment is continued until at least the liquid Al phase is substantially removed. A short cycle (< 30 minutes) may be possible for this step if all that is needed is to drive the liquid Al into the Ni matrix. At 1,000 °C, one temperature suitable for making nickel aluminide (NiAl) foils, aluminum (Al) is in liquid state since the melting point of Al is 660 °C. Al atoms diffuse into the nickel (Ni) matrix to form intermetallic phases. For working embodiments, for 0.010" thick composite foil 0.006" total Al thickness, 1 hour of annealing time was long enough for liquid Al to diffuse into the Ni matrix. The stated aluminum thickness is divided as two

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layers on either side of the Ni so that the amount of time needed to absorb the Al into the Ni matrix is for one half of these amounts of Ni. Similarly, a 30-minute annealing time was sufficient for Al atoms to diffuse into the Ni matrix for 0.005" thick composite foil (0.003" of Al). For the 0.0025" thick composite foil, no data is available for an annealing time of less than 5 30 minutes. However, after 30 minutes of annealing time, as expected, there was no Al left for this thickness. The annealing time required for 0.0025" thick composite foil can be approximated by plotting the data and extrapolating from the data discussed above. Therefore, it can be estimated that the annealing time required for the 0.0025" thick composite foil is about 15 minutes. These annealing times include both heating and cooling times. The heating times 10 for these heat treatments were 100 minutes (the heating rate was 10 °C/min). The cooling times were not recorded.

In any event, the initial synthesis time is minimized so that synthesis of the intermetallic can be finished during a subsequent diffusion bonding cycle. Also, if patterning dominates costs, only tack bonding may be done initially and so patterning in a ductile state by blanking or 15 some other lower cost patterning option occurs.

The blanks are patterned by a machining technique, such as laser machining or ram EDM. Perforation might be used in this step if the blank is significantly larger than the laminae.

A Ni thin film or laminae, on the order of a few microns, is applied to the surface of the annealed foil prior to bonding. Electroless Ni can be applied to the surface in a high-volume 20 bath. Ni plating also can be done before the patterning step.

Diffusion brazing and heat treatment of the laminae are then performed in tandem. Cycle time reduction is possible by using composite foils and minimizing the thickness of the Ni-plated layer. Heat treatment is performed to normalize the microstructure of the foil. The foil may not be completely converted to its final normalized microstructure. This could be 25 performed in either a hot isostatic press (for large substrates) or in a high temperature clamp (using coefficient of thermal expansion [CTE] mismatch).

### Example 13

This example concerns an alternative embodiment for high-volume fabrication of NiAl 30 intermetallic microchannel arrays using roll bonding to maintain the ductility of the composite

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foils so that economical methods (such as blanking) can be used to pattern the foil. High-purity aluminum (Al 1100; 99% aluminum) and nickel (Ni, 200 grade annealed material, 99% nickel) foils were obtained commercially. The thicknesses of the starting materials were selected to provide the atomic ratio 1:1 of Ni to Al (thickness ratio of Ni to Al is 2:3). The elemental foils are roll bonded to a desired thickness to provide intimate contact between the two elements. The roll bonded foil is patterned by a machining or forming technique, such as laser machining or blanking. Perforation might be used to facilitate separation of the patterned foils from the roll once the roll is converted to an intermetallic. Heat treatment is performed to initiate reactive diffusion and to begin normalizing the microstructure of the foil. The foil may not be completely converted to its final normalized microstructure. A tradeoff exists between making the foil too brittle for handling and providing enough elastic modulus to provide the stiffness for the foil in subsequent bonding steps. This tradeoff is controlled by the length and conditions of the heat treatment, which will result in some distribution of aluminide phases within the foil. Some phases are stiffer and more brittle than others. This step can be done in a batch step or on a continuous basis within a conveyORIZED furnace. However, the heat treatment requires that slight pressure be applied to the foil during conversion to prevent warpage due to phase transformation. This pressure could be applied by the pressure plates on a second conveyor.

A thin nickel film having a thickness of a few microns can be applied to the surface of the annealed foil prior to bonding. Electroless Ni could be applied to the surface in a high-volume bath.

Annealed foils are cut off from the roll using laser machining, wire EDM or some such process selected to minimize cracking. Laser machining and EDM both have been found to machine these foils without cracking. Laser machining likely is preferred because of its enhanced production rate, although wire EDM would be more precise. The individual laminae are automatically stacked and aligned as they are processed. More specifically, the Ni-plated patterned foils are stacked and then reactive diffusion bonded to build the final microchannel arrays. This can be done using a batch process or using a conveyORIZED furnace with a high-temperature clamp based on the difference in CTE between the clamp and the NiAl material.

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**Example 14**

This example describes a process for making a NiAl microchannel array having three microchannels 3810  $\mu\text{m}$  wide and 16,510  $\mu\text{m}$  long. Laminae for a parallel flow heat exchanger are illustrated by FIG. 22. The height of the channels was determined after bonding because  
5 height increases due to the addition of filler metal between the foils. The overall dimensions of the devices were 13,970  $\mu\text{m}$  wide and 25,400  $\mu\text{m}$  long.

Due to different densities and phase changes during the transformation from elemental Ni and Al foils to NiAl foil, volumetric contraction takes place (Ni, Al, and NiAl have a density of 8.90, 2.70, and 5.86  $\text{g}/\text{cm}^3$ , respectively). This dimensional instability was noticed during the  
10 conversion of elemental foils to intermetallic. These dimensional changes show another difficulty in fabricating intermetallic micro devices from the elemental foils as previously proposed by Alman *et al.* (2001) and Paul *et al.* (2000; 2002), and it suggests a requirement of a new fabrication procedure for building the intermetallic microchannel devices.

Three general steps are involved in microlamination: lamina patterning, laminae  
15 registration, and laminae bonding. The present fabrication method starts from fully developed NiAl foils. Although the NiAl foils are not commercially available, they can be synthesized from elemental Ni and Al foils as described herein. To make an NiAl foil with 127  $\mu\text{m}$  nominal thickness, an elemental Ni foil with a thickness of 50.8  $\mu\text{m}$  was sandwiched by two Al foils, each with a thickness of 38.1  $\mu\text{m}$ . The foils were then tack bonded at 500  $^{\circ}\text{C}$ , 575 psi, at  
20  $1 \times 10^{-4}$  mbar for 15 minutes to obtain an intimate contact between these two elements. After tack bonding, thin layers of intermetallic material are produced at the interface of the two elemental foil. Tack bonding provides the energy necessary to produce the interfacial boundary between the two foils. Beyond this step, it is no longer necessary to provide bonding pressure to anneal the foils. The tack bonded foil was then heat treated at 1,000  $^{\circ}\text{C}$  for 16 hours to  
25 transform the elemental Ni and Al into intermetallic NiAl. Without further phase transformations of the elemental foils, dimensional accuracy of the devices is improved with this new fabrication procedure. In this development, the NiAl foils with 127  $\mu\text{m}$  nominal thickness were cut into desired patterns using 532-nm laser micromachining. Cracking due to the machining technique was not observed. Ultrasonic cleaning in a solvent as typically used  
30 with conventional materials, such as stainless steel, is not applicable to NiAl foils, as such foils

will be cracked along the grain boundaries during ultrasonic cleaning. In applying reactive diffusion, 99.99% pure Ni foils each with a thickness of 7.5  $\mu\text{m}$  were used as the filler metals to achieve bonding of the NiAl foils. They were patterned using a 532 nm laser as well. The dimensions of the patterned filler metal foils were the same as those of the channel. After the  
5 patterning step, the filler metals were cleaned using acetone, methanol, and de-ionized water to remove grease from the foil's surfaces.

All laminae were then registered to the designed sequence. In this step, a graphite fixture with edge alignment was employed.

10 Finally, the registered laminae were diffusion bonded at 1000 °C, 20.7 MPa, for 8 hours in a vacuum environment.

It is desired to employ the micro channel array devices in a laminar flow regime to obtain superior heat transfer performance from the devices. A working fluid (water) was fed into the devices with Reynolds numbers less than 50, which is in the laminar flow regime of microchannel ( $\text{Re}_{D_h} < 1000$ ) (Obot, 2000). To verify whether or not the flow in the micro  
15 channel is fully developed, entrance length ( $l_e$ ) of the flow is compared to the actual length ( $l$ ) of the conduit.

For laminar flow; 
$$\frac{l_e}{D_h} \approx 0.06 \text{Re}_{D_h} \quad (\text{White, 2002})$$

In this experiment, the selected maximum  $\text{Re}_{D_h}$  is 50; therefore, the maximum  $l_e/D_h$  ratio is 3.

For the actual conduit,  $l/D_h$  is equal to 16510/260.76 or 63.315. Hence the entrance region takes  
20 up the fraction:

$$\frac{l_e}{l} = \frac{3}{63.315} = 0.047 = 4.7\%$$

This is a small percentage, thus it is reasonable to assume that the flow in the micro channel is fully developed laminar flow. Therefore, the eligible volumetric flow rate ( $n \cdot q = Q$ ) for the laminar flow can be determined from:

25 
$$Q = \frac{A \nu \text{Re}_{D_h}}{D_h} = \frac{wh \nu \text{Re}_{D_h}}{D_h}$$

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By substituting numerical values of these parameters, the flow rate supplied to the device can be calculated. Using a Reynolds number of 50, the maximum volumetric flow rate to obtain laminar flow in the conduits is about  $2.988 \times 10^{-7} \text{ m}^3/\text{s}$ . In this example, the Reynolds numbers used were 50, 40, 30, 20, and 10.

5 To perform the pressure drop test, water was supplied to the device by a syringe pump at required flow rates. The pressure drop across the device was measured by the pressure transducer before sending out the signal to the process meter. The operable ranges of the pressure transducer and process meter are 0 – 25 psi, and the resolution of the process meter is 0.01 psi.

10 After bonding, the NiAl micro heat exchangers were tested for their bond quality using a leak test. The purpose of the leak test is to determine whether the devices are hermetically bonded or not, which is an important factor for fluidic devices. Also, leakage was reported as a major barrier in building intermetallic micro channel arrays (Alman *et al.*, 2001; Paul *et al.*, 2000; 2002). To perform the leak test, the device was connected to an air supply. Silicone and  
15 rubber glue were used to seal at all connection points as well as to provide some flexibility between the device and the tubes to prevent cracking of the NiAl. Air was fed into the inlet port of the device while the other port was plugged and was pressurized in the device. Since the device was immersed in water, leakage of the device can be observed easily from air bubbles. The air pressure was gradually increased until leakage from the device was found. The last air  
20 pressure was then recorded.

The device was observed on its cross section to verify the bond quality and to double check the reliability of the leak test. The device was drilled on the end plate by a 532-nm laser and then molded in low-viscosity epoxy resin. The mold was immediately placed in a vacuum bowl to evacuate the air bubbles inside the device, and consequently to fill the device with the  
25 resin. The laser-drilled holes assisted the flow of the resin into the device. After the resin hardened, the resin-filled device was sectioned and polished to observe the bond quality as well as the flatness of the fins.

Three NiAl microchannel arrays were fabricated and tested in this study. Results from the pressure drop tests are shown in FIG. 22. In general, the actual pressure drops were higher  
30 than the theoretical values. The higher pressure drops in the devices were due to the

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dimensional variation in the microchannels that deviates from the theoretical assumption in which the flow takes place in a uniform passage. The difference in pressure drop from theoretical value was more distinct at high  $Re_{D_h}$  numbers because at these numbers the flow of water also deviated from the assumption of fully developed condition more than at low

5  $Re_{D_h}$  numbers. On the average, the experimental pressure drop was 19.80% higher than the theoretical value.

In the next step, all three pieces of micro heat exchangers were leak tested, and the maximum air pressures were recorded. The maximum pressure supplied to the systems ranged from 10-12 psi before the test was stopped. During the test, no air bubble from the devices was

10 observed. However, the air pressure was not further increased because air bubbles emerged from the connection between the air tube and the device. To leak test at higher pressures, a better inlet and outlet port of the device is required to obtain a good connection between the device and the outside fluidic system.

A cross section of a microchannel array heat exchanger fabricated according to a

15 previous example is illustrated by FIG. 24. FIG. 25 illustrates the result from this example. The leakage problem was overcome by the proposed bonding technique. Under an optical microscope at 500X magnification, the phases presented at the bond lines can be reasonably distinguished from their color. The phase presented at the center of the bond line was  $Ni_3Al$  intermetallic compound, and the outer shade was the intermediate phase between  $Ni_3Al_3$  and

20  $NiAl$ . Small voids were also present at the interface between the foils and the filler metal. However, they did not cause leakage of the device. These voids could be eliminated by improving the foil smoothness.

Using the proposed fabrication technique, significant improvement on the quality of the  $NiAl$  microchannel array heat exchanger was achieved. Fin warpage was reduced to an

25 acceptable magnitude by using the fully homogenized  $NiAl$  foil as the starting material, while the leakage of the device was solved by reactive diffusion bonding.

### Example 15

This example describes a fabrication procedure for producing  $NiAl$  intermetallic

30 microchannel arrays. Aluminum (Al) and nickel (Ni) foils [aluminum alloy 1100 (99% Al);



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nickel foil, 200 grade annealed material (99% Ni). The thicknesses of the starting materials were calculated to provide the atomic ratio 1:1 of Ni to Al (volumetric ratio of Ni to Al is 2:3. The elemental foils were stacked in alternate sequence of Al-Ni-Al for an individual composite lamina. Ni was positioned in the middle to avoid Kirkendall porosity problems in the Al foil.

5 A single composite lamina was tack bonded using diffusion bonding to provide an intimate contact between the two elements. A fixture is used in this step. Each composite lamina is separated from each other by a plate, such as a graphite plate, to prevent bonding. The tack bonding conditions for these elemental foils were 500 °C, 575 psi, and 15 minutes holding time. Tack bonding was done in a vacuum of about  $1 \times 10^{-4}$  mbar. After tack bonding, very thin  
10 layers of intermetallic material are produced at the interface of the two elemental foils. This tack bonding procedure provides the necessary energy to produce the interfacial boundary between the two foils. Beyond this step, it is no longer necessary to provide bonding pressure to anneal the foils. Unbonded areas, typically at the edges, are trimmed by removing the blanks from the furnace and using a shear to remove excess material.

15 Composite foils were reinserted into the furnace and heat treated at 1,000 °C for 16 hours under slight bonding pressure applied by the weight of graphite plates. A graphite fixture is used for the annealing purpose. Graphite plates were used to separate the composite foils from one another and to prevent the foils from warping (due to the slight applied pressure from their weight). This heat treatment process is operated under a vacuum of about  $1 \times 10^{-4}$  mbar.  
20 The purpose of this heat treatment step is to stiffen the foils by wholly or partially transforming the elemental aluminum and nickel into intermetallic phases and to minimize dimensional change in the z-axis due to bonding pressure during the phase transformation.

The annealed foils were removed from the furnace and cut into patterns using either 266 or 532 nm laser micromachining. The literature has revealed that EDM of NiAl is possible as  
25 an alternative to laser machining.

The patterned foils were stacked and then reactive diffusion bonded to build microchannel arrays. Commercially pure (99.99%) Ni foil with a thickness of 7.5  $\mu\text{m}$  was used as the filler metal. The foils were bonded at 800 °C under 3,000 psi applied pressure for 8 hours. A vacuum of about  $1 \times 10^{-4}$  mbar also was used in this diffusion bonding process.  
30 Another graphite fixture is used in this step.

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FIG. 26 is a micrograph illustrating the ability to control dimensions and eliminate warpage on the fins of a microchannel array having an aspect ratio of 100:1 and about a 125 micron channel height. FIG. 27 is a graph establishing the atomic percent of Ni and Al in devices made according to this example. Finally, FIG. 28 is a cross section (8X) of a leak-tight,  
5 28:1 aspect ratio, NiAl microchannel array device made according to this example.

Having illustrated and described the principles of the invention in exemplary embodiments, it should be apparent to those skilled in the art that the illustrative embodiments can be modified in arrangement and detail without departing from such principles. In view of the many possible embodiments to which the principles of the invention can be applied, it  
10 should be understood that the illustrative embodiments are intended to teach these principles and are not intended to be a limitation on the scope of the invention. We therefore claim as our invention all that comes within the scope and spirit of the following claims and their equivalents.

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**WE CLAIM:**

1. A method for making a structure, at least a portion of which is intermetallic, the method comprising:
  - 5 providing at least one machinable intermetallic lamina;
  - machining the at least one machinable intermetallic lamina to form a machined intermetallic lamina;
  - stacking and registering the at least one machined intermetallic lamina with at least one other lamina selected from the group of patterned lamina, non-patterned lamina and
  - 10 combinations thereof, thereby forming a registered stack; and
  - processing the registered stack to make an intermetallic structure.
2. The method according to claim 1 where the intermetallic lamina is a nickel  
15 aluminide.
3. The method according to claim 2 where the nickel aluminide is NiAl.
4. The method according to claim 2 where the nickel aluminide is Ni<sub>3</sub>Al.
- 20 5. The method according to claim 1 where the intermetallic lamina is an iron aluminide.
6. The method according to claim 5 where the iron aluminide is FeAl.
- 25 7. The method according to claim 5 where the iron aluminide is Fe<sub>3</sub>Al.
8. The method according to claim 1 where the intermetallic lamina is a titanium aluminide.
- 30 9. The method according to claim 8 where the titanium aluminide is TiAl.

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10. The method according to claim 8 where the titanium aluminide is  $Ti_3Al$ .

11. The method according to claim 1 further comprising adding at least one  
5 bonding lamina or layer to the registered stack to facilitate bonding between a first intermetallic lamina and a second intermetallic lamina.

12. The method according to claim 11 where the bonding lamina is substantially  
pure nickel.  
10

13. The method according to claim 12 where the bonding lamina has a thickness of  
from about 5 to about 10 microns.

14. The method according to claim 1 where machining is a technique selected from  
15 the group consisting of lithography, laser ablation, electrochemical processes, chemical etching, plasma etching, mechanical cutting, hydraulic processes, solid abrasion, particle beam, ultrasonic processes; electromagnetic processes, including momentum transfer and energy transfer from any portion of the electromagnetic spectrum, wire and ram electrodischarge (EDM), waterjet and abrasive waterjet, precision plasma cutting, and combinations thereof.  
20

15. The method according to claim 1 where providing comprises procuring a  
patterned lamina or lamina blank.

16. The method according to claim 1 further comprising providing at least a second  
25 lamina in addition to the at least one machinable intermetallic lamina, the second lamina comprising at least a first metal layer and a second metal layer.

17. The method according to claim 16 where each of the first and second metal  
layers comprises a substantially pure element prior to heat treatment.  
30

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18. The method according to claim 17 where the second lamina comprises three metal layers.

19. The method according to claim 18 where one of the layers comprises an  
5 element different from the other two layers.

20. The method according to claim 19 where one of the layers is selected from the group consisting of substantially pure iron, nickel, titanium and aluminum.

10 21. The method according to claim 18 wherein two of the layers are substantially pure aluminum, and one layer is substantially pure nickel.

22. The method according to claim 18 where two of the layers are substantially pure aluminum, and one layer is substantially pure titanium.  
15

23. The method according to claim 1 where coupling is accomplished using an adhesive applied between two or more laminae.

24. The method according to claim 17 where processing comprises vacuum heating  
20 at a temperature and for a length of time sufficient to form an intermetallic.

25. The method according to claim 16 where processing further comprises liquid-phase bonding.

25 26. The method according to claim 16 where processing further comprises diffusion bonding.

27. The method according to claim 1 wherein the intermetallic structure includes one or more catalysts operatively associated therewith.  
30

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28. An intermetallic device made according to the method of claim 1.

29. A device comprising a patterned intermetallic portion.

5           30       The device according to claim 29 selected from the group consisting of  
micromechanical systems, microelectromechanical systems, miniature energy and chemical  
systems, microthermal systems, microthermomechanical systems, cryocoolers, Stirling cycle  
cryocoolers, heat pumps, compressors, thermal compressors, refrigerators, heat engines, valves,  
nozzled valves, ink jet print head valves, fuel cells, fuel combustors, fuel processors,  
10   electromagnetic systems, electromagnetically enhanced systems, magnetic systems,  
magnetically enhanced systems, and systems comprising one or more of these devices.

          31.       A method for making an intermetallic structure, comprising:  
                  providing a plurality of stacked and registered laminae; and  
15               heat processing the stacked and registered laminae to form a monolithic structure  
comprising an intermetallic.

          32       The method according to claim 31 where at least one of the plurality of stacked  
and registered laminae is a patterned intermetallic lamina.

20           33.       The method according to claim 31 where at least one lamina of the plurality of  
stacked and registered laminae comprises at least a first metal layer and a second metal layer.

          34       The method according to claim 33 where the at least one lamina is patterned  
25   prior to heat processing.

          35       The method according to claim 31 where at least a first lamina of the plurality of  
stacked and registered laminae is a patterned intermetallic lamina, and where at least a second  
lamina of the plurality of stacked and registered laminae comprises at least a first metal layer  
30   and a second metal layer.

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36 The method according to claim 35 where the second lamina is patterned prior to heat processing.

5 37 The method according to claim 31 where at least two adjacent lamina are connected by at least one post.

38 The method according to claim 31 further comprising operatively associating at least one catalyst with the structure.

10

39. The method according to claim 32 where the intermetallic lamina is patterned using a technique selected from the group consisting of lithography, laser ablation, electrochemical means, chemical etching, plasma etching, mechanical cutting, hydraulic means, solid abrasion, particle beam, ultrasonic means; electromagnetic means, wire and ram  
15 electrodischarge (EDM), waterjet and abrasive waterjet, precision plasma cutting, and combinations thereof.

40. The method according to claim 32 where the intermetallic portion is a nickel aluminide.

20

41. The method according to claim 32 where the intermetallic portion is an iron aluminide.

42. The method according to claim 32 where the intermetallic portion is a titanium  
25 aluminide.

43. The method according to claim 31 where at least one of the lamina in the registered stack of laminae comprises a metal selected from the group consisting of aluminum, nickel, titanium, molybdenum, tantalum, copper, gold, silver, lead, tin, iron, antimony,  
30 magnesium, manganese, bismuth, germanium, tungsten, binary alloys thereof, binary

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intermetallics thereof, ternary alloys thereof, ternary intermetallics thereof, and combinations thereof.

5

44. The method according to claim 43 where the metal is a metal foil.

45. The method according to claim 31 where the stacked lamina comprise plural intermetallic foils.



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**METHOD FOR MAKING DEVICES HAVING INTERMETALLIC  
STRUCTURES AND INTERMETALLIC DEVICES MADE THEREBY**

**ABSTRACT OF THE DISCLOSURE**

5           A method and system for making an intermetallic structure are disclosed. The structure  
is made from lamina blanks, which comprise multiple layers of metals which are patternable, or  
intermetallic lamina blanks that are patternable. Lamina blanks are patterned, stacked and  
registered, and processed to form an intermetallic structure. The advantages of a patterned  
monolithic intermetallic structure include physical characteristics, such as melting temperature,  
10 thermal conductivity, and corrosion resistance. Applications are broad, and include among  
others, use as a microreactor, heat recycling device, and apparatus for producing superheated  
steam. Monolithic intermetallic structures may contain one or more catalysts within the internal  
features.

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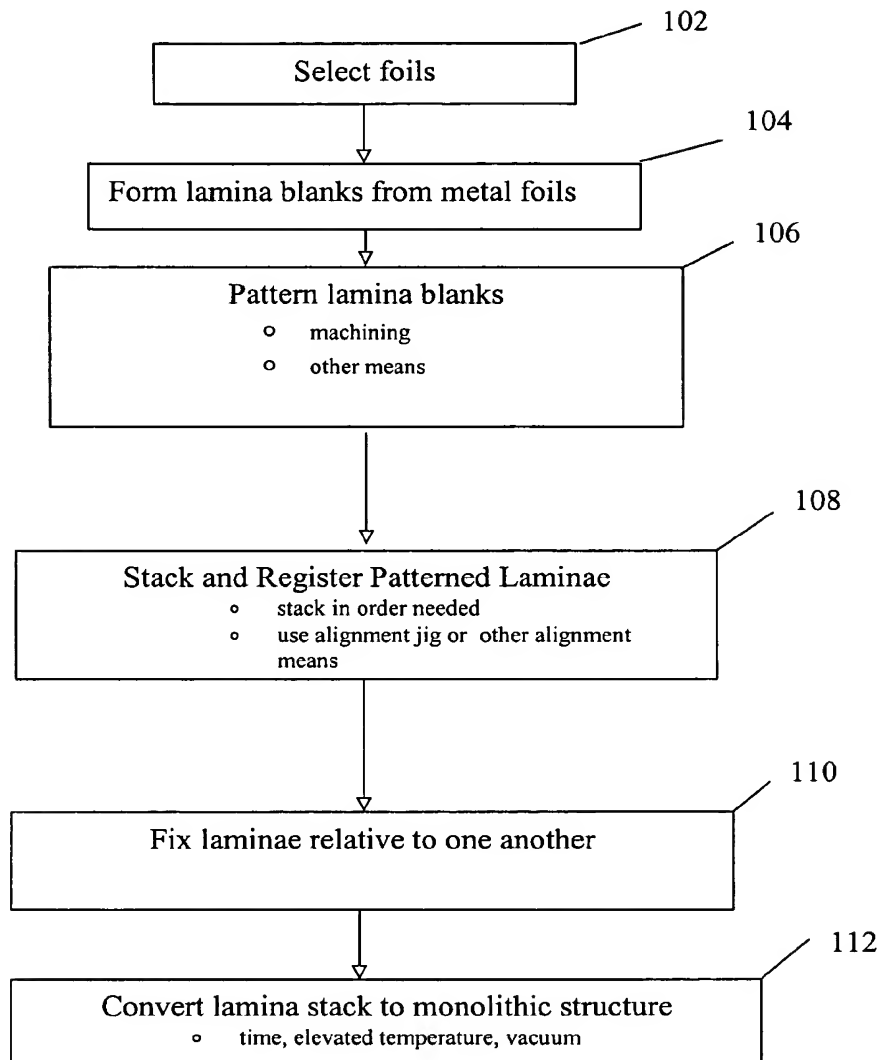
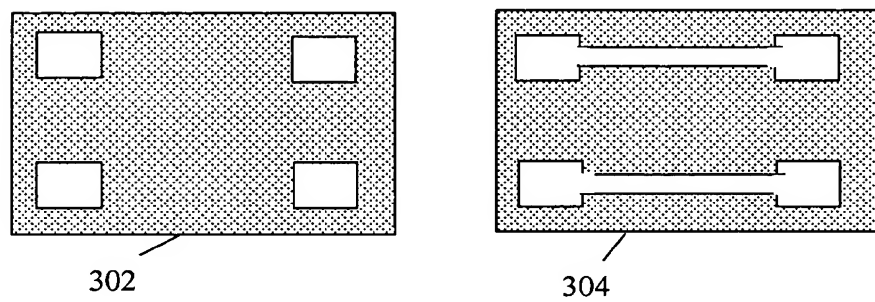
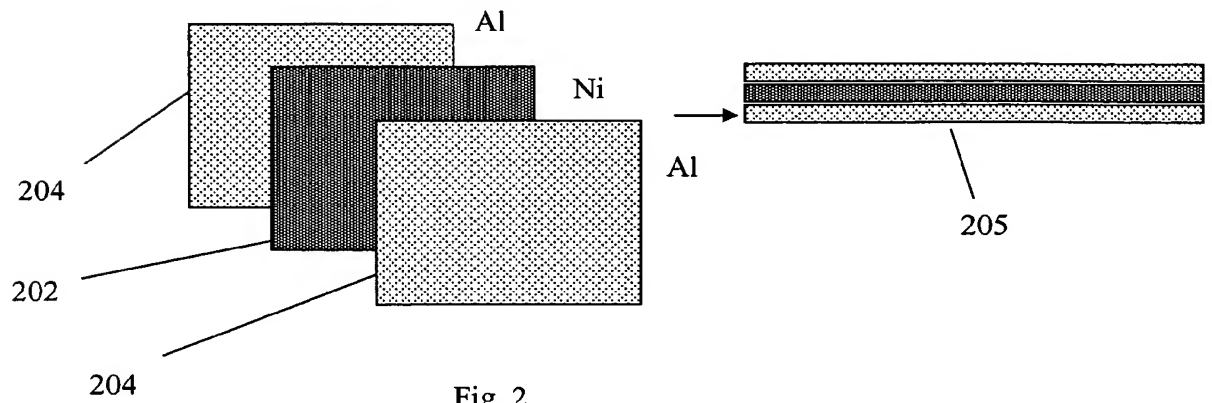


Fig. 1

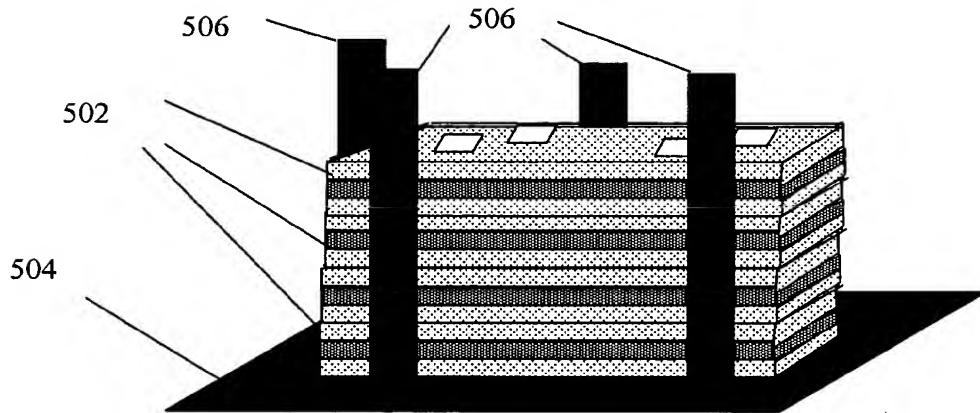
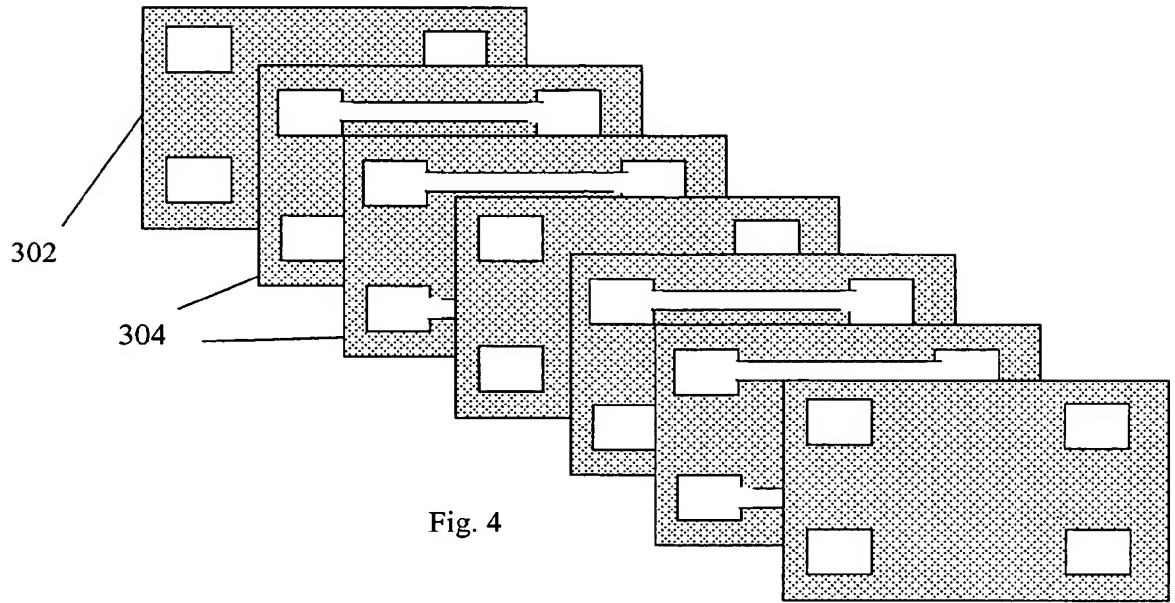
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Our Ref. No. 245-68071  
For: Method for Making Devices Having  
Intermetallic Structures and Intermetallic  
Devices Made Thereby  
Inventor(s): Paul et al.  
Express Mail Label: EV339206216US  
Mailed: March 17, 2004



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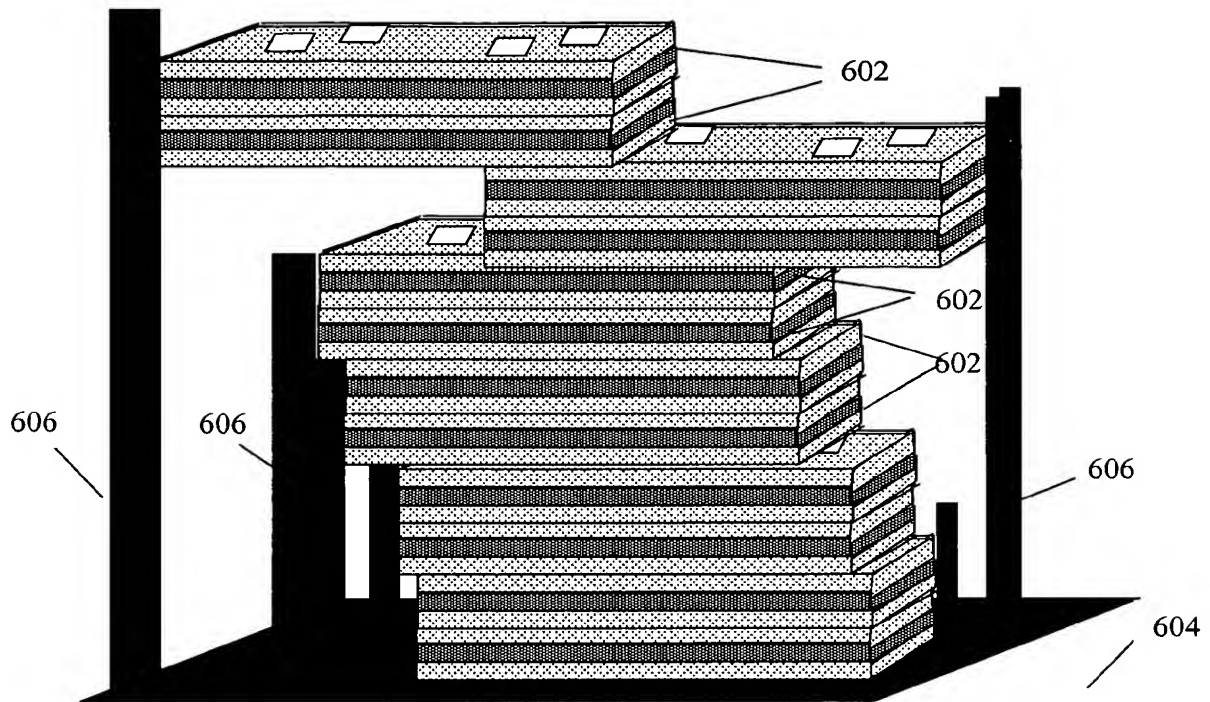


Fig. 6

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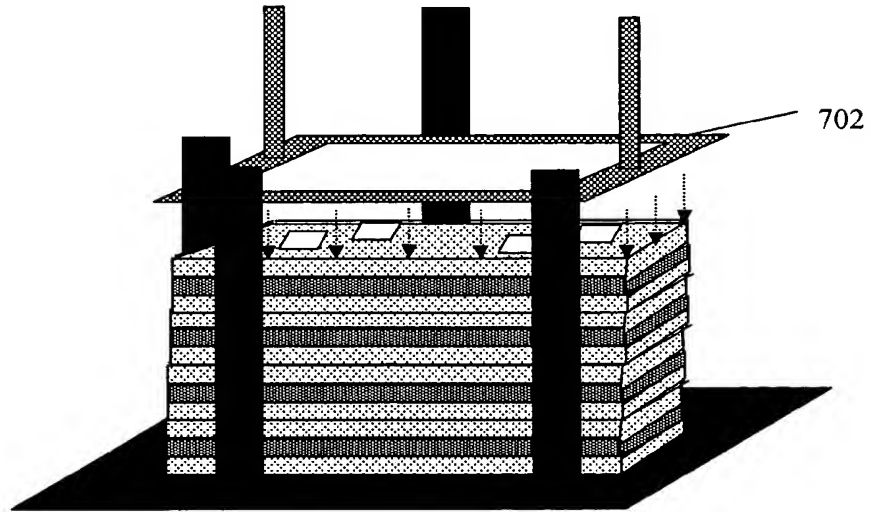


Fig. 7

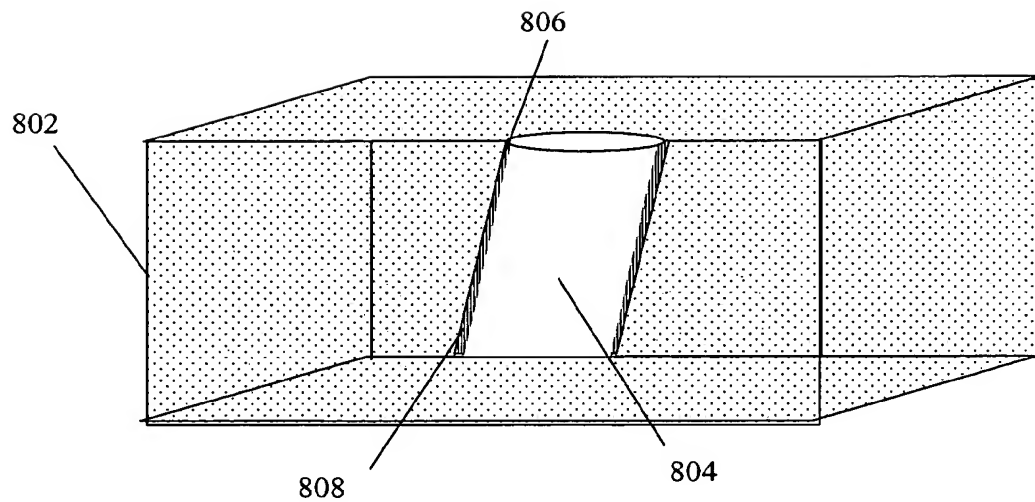
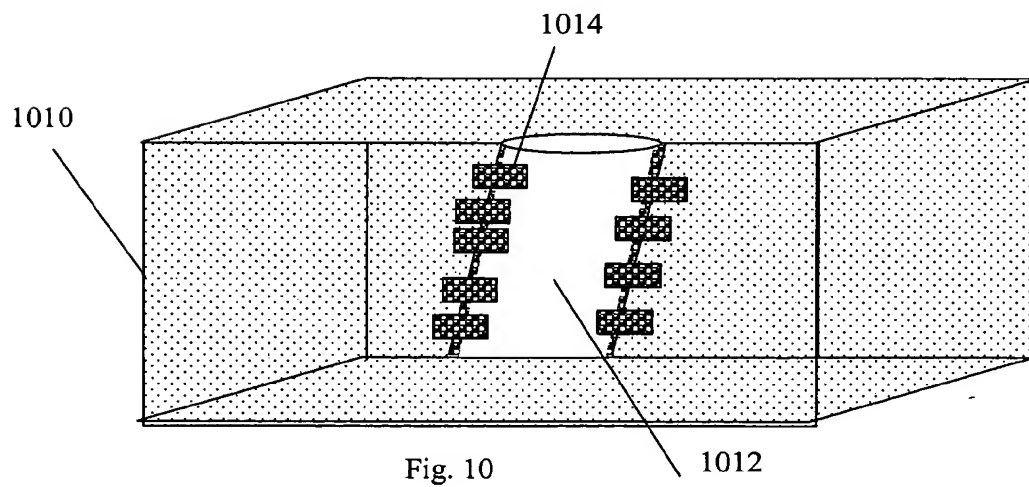
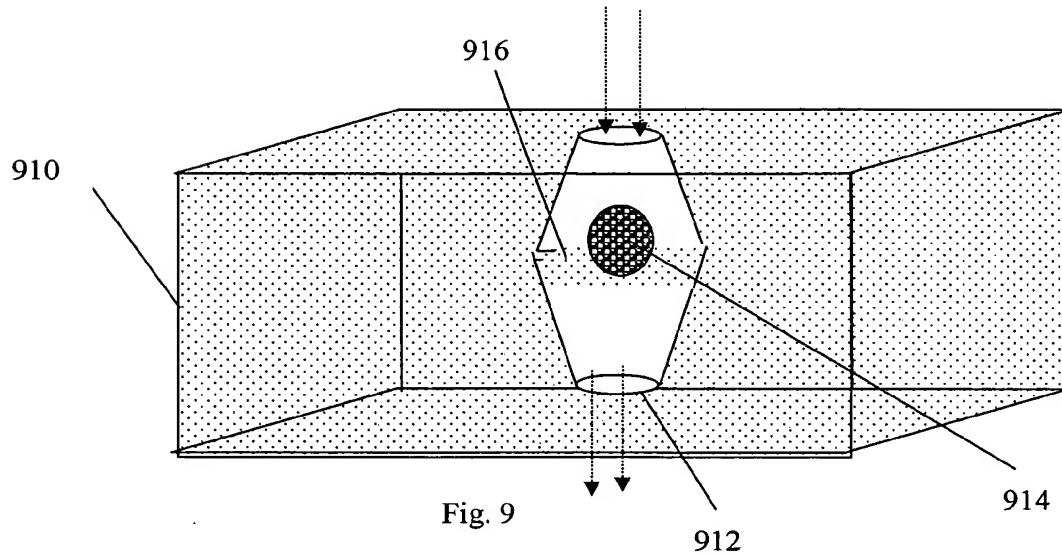


Fig. 8

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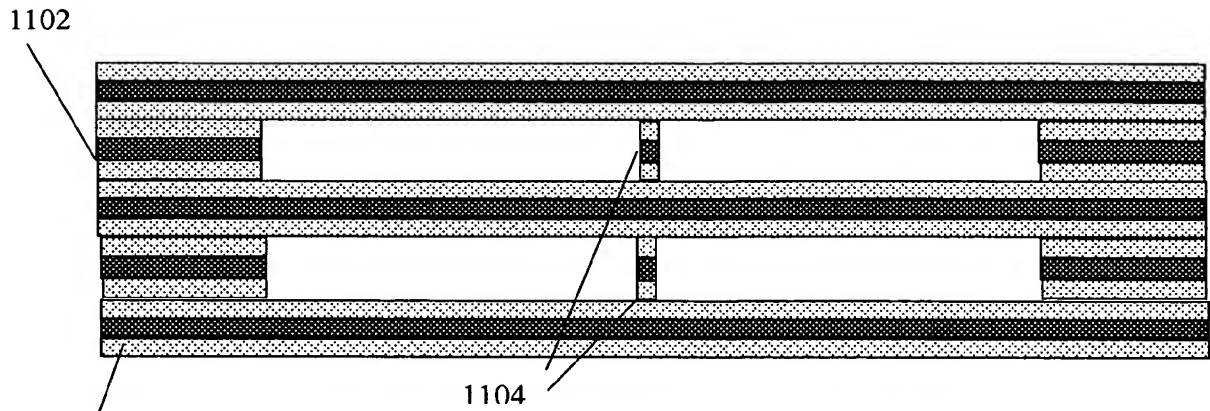


Fig. 11A

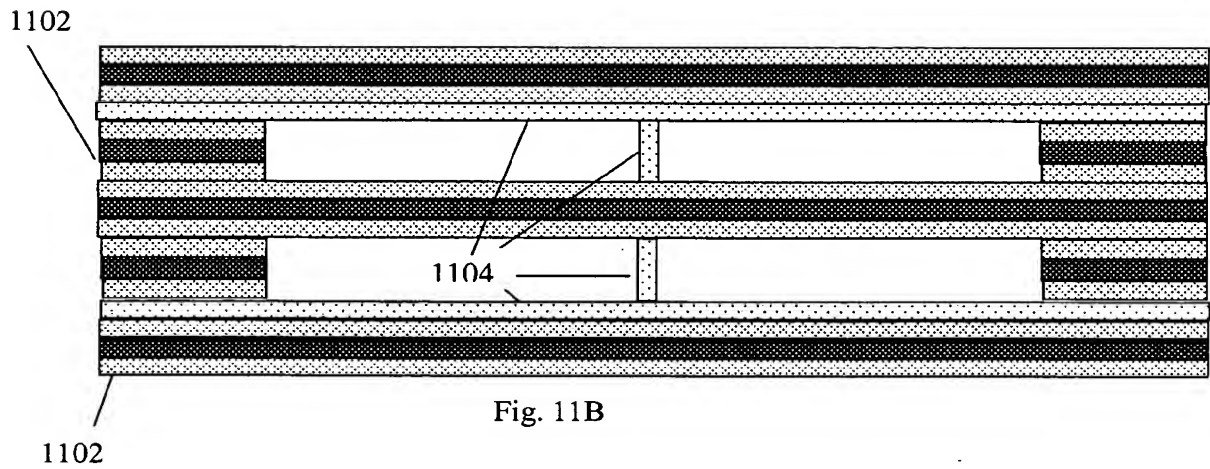
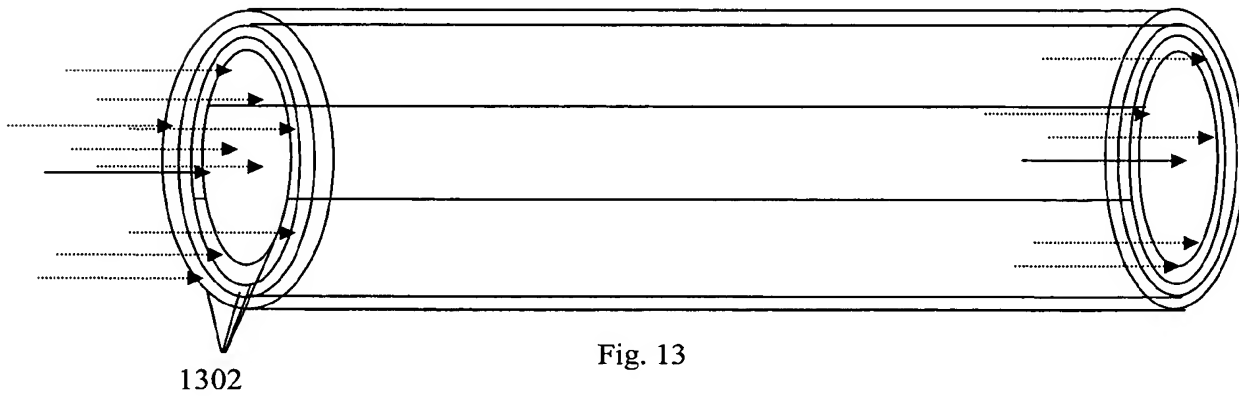
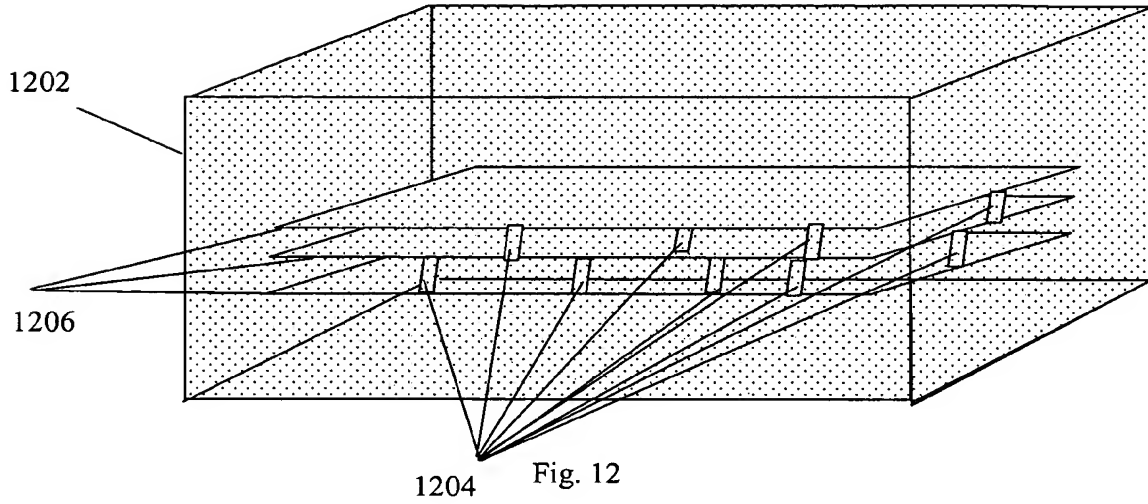


Fig. 11B



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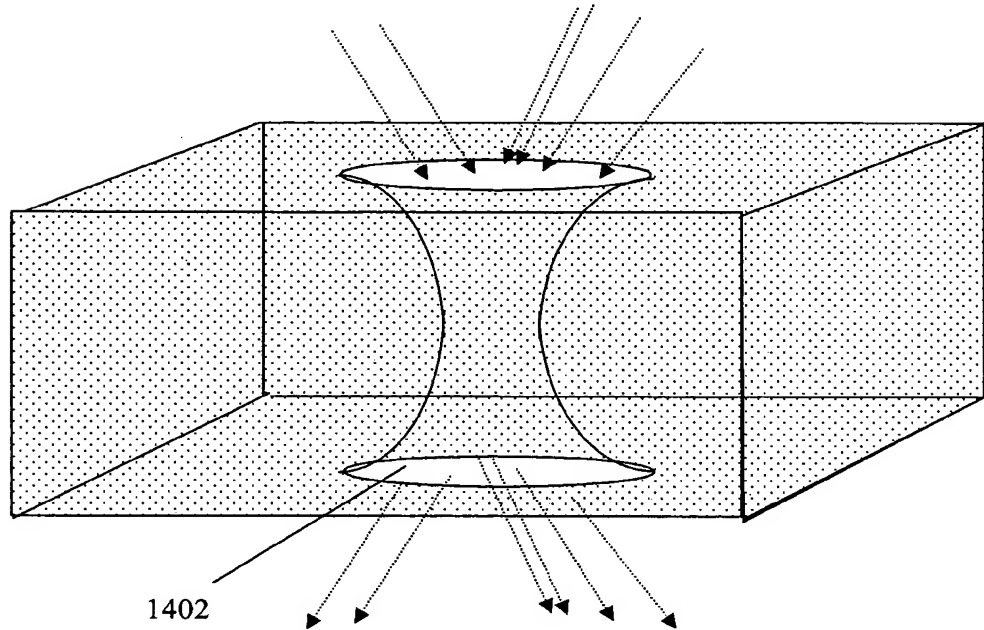


Fig. 14

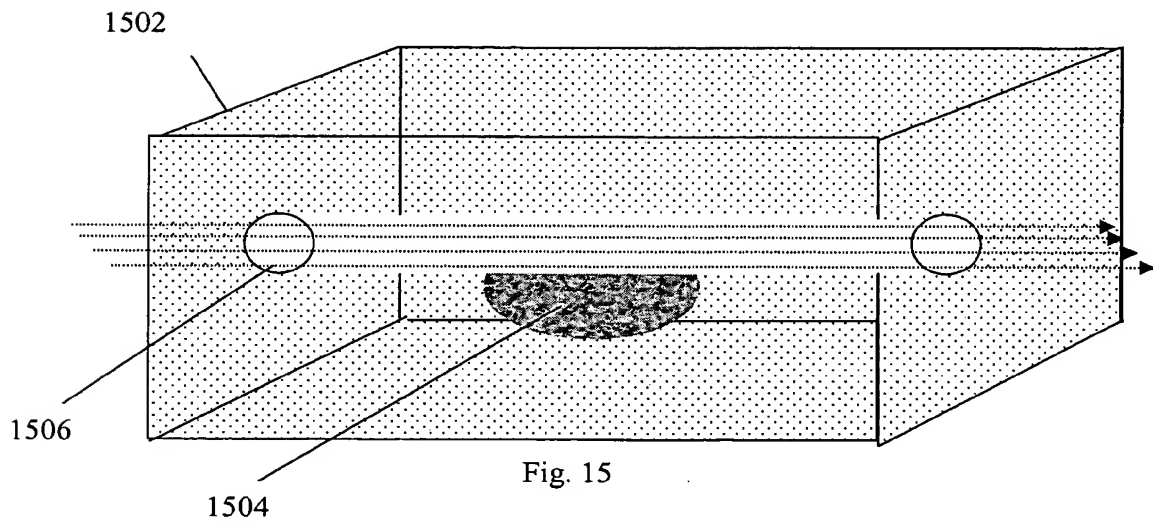


Fig. 15

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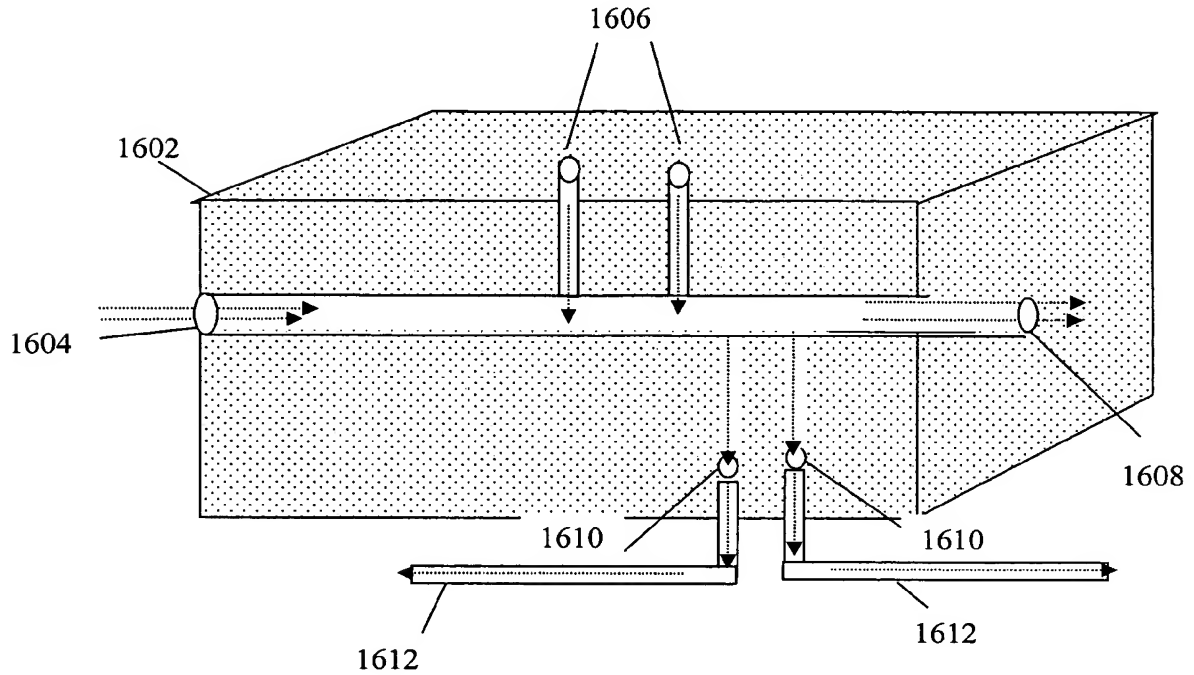


Fig. 16

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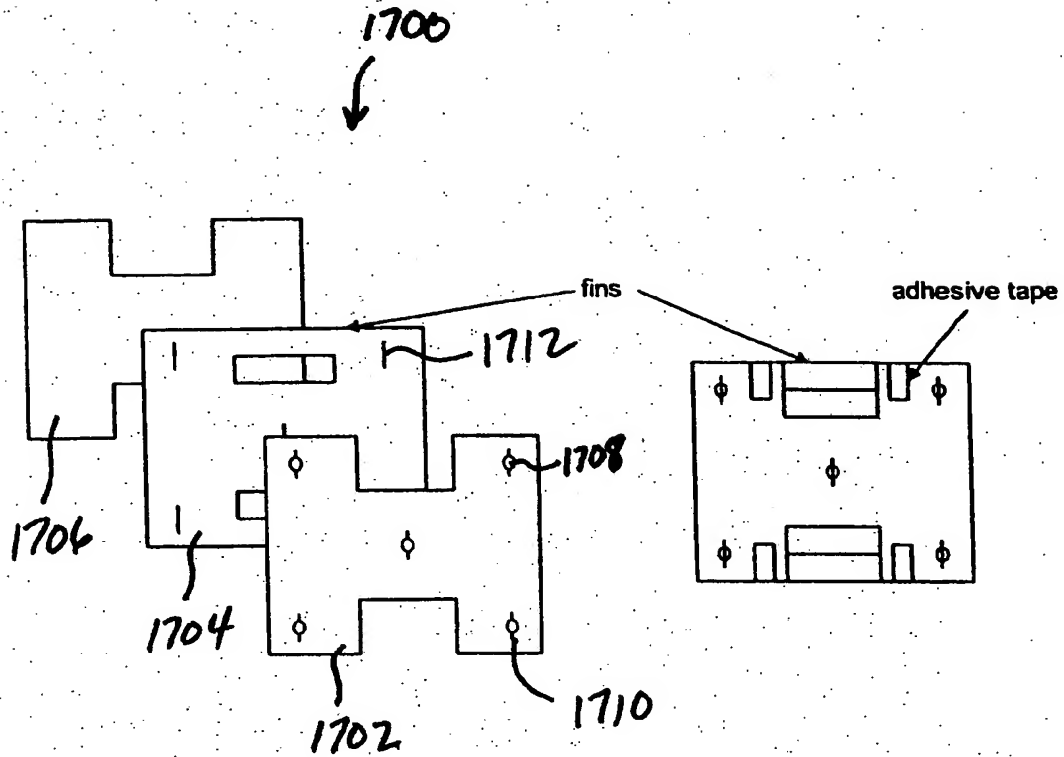


Fig. 17

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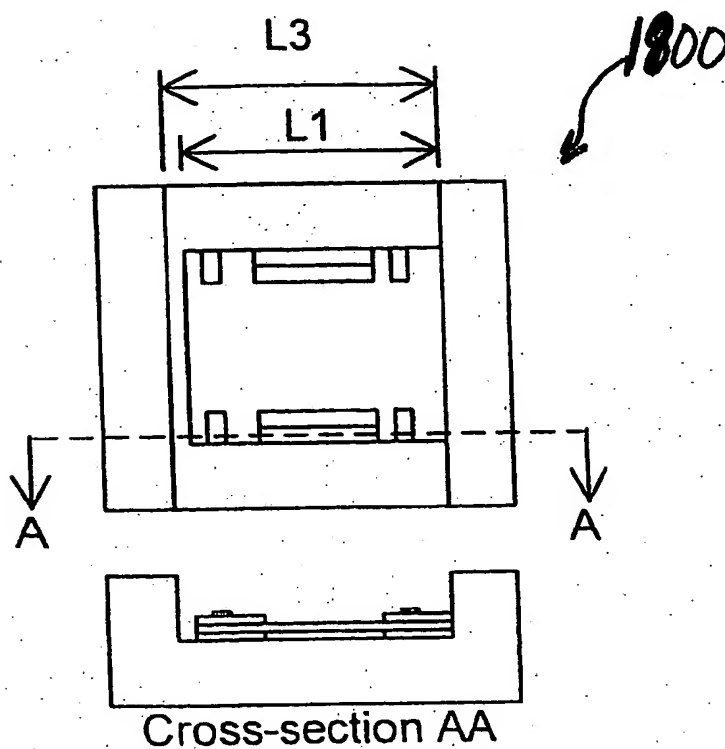


Fig. 18

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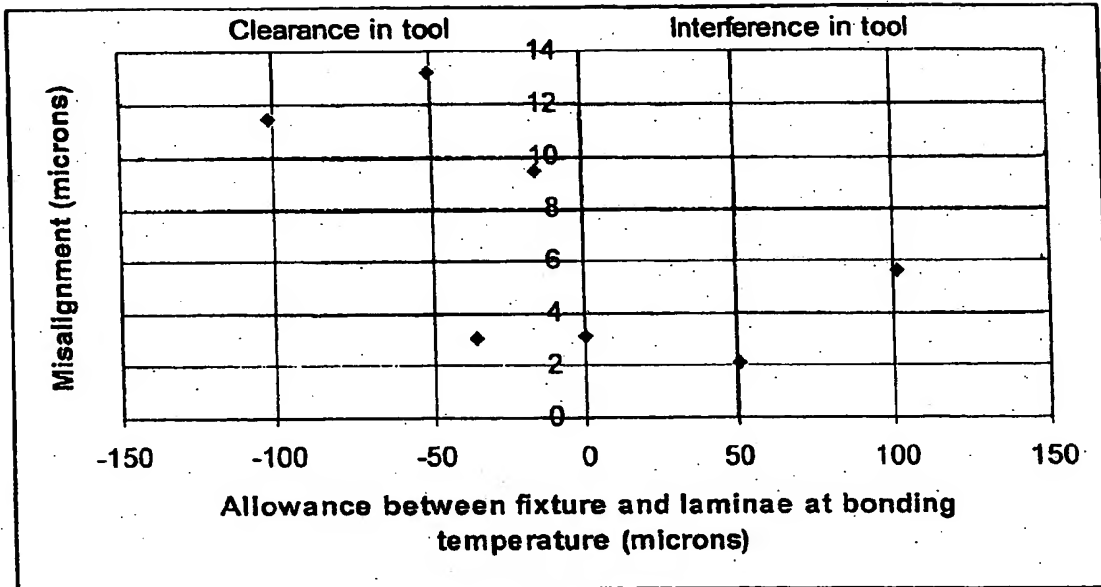
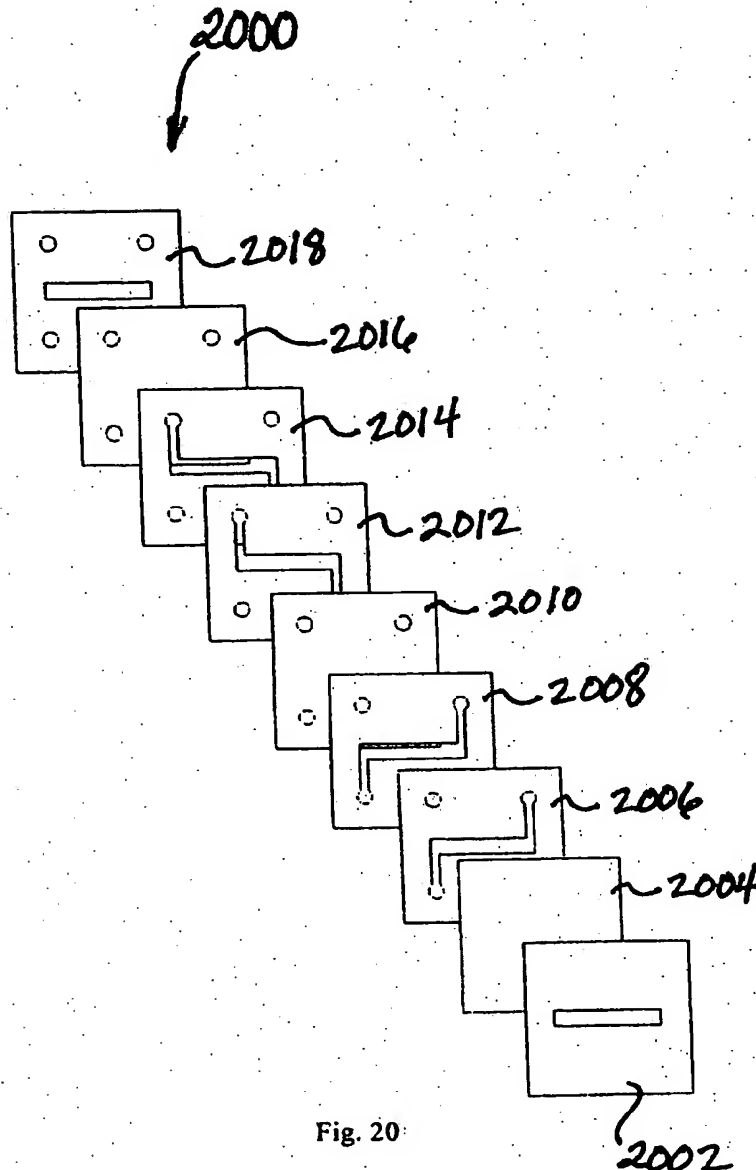


Fig. 19

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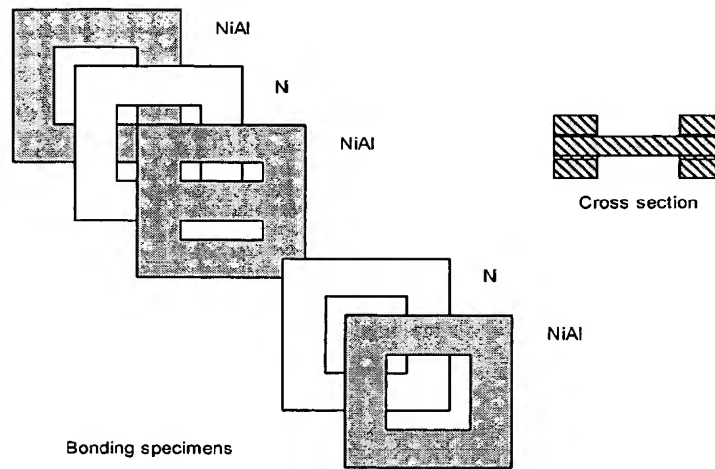
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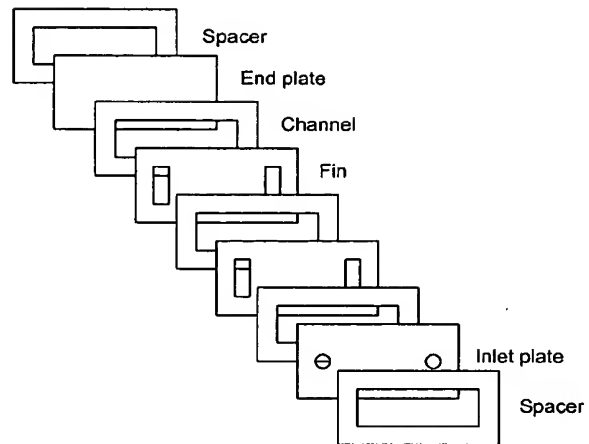
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**Fig. 21**

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**Fig. 22**

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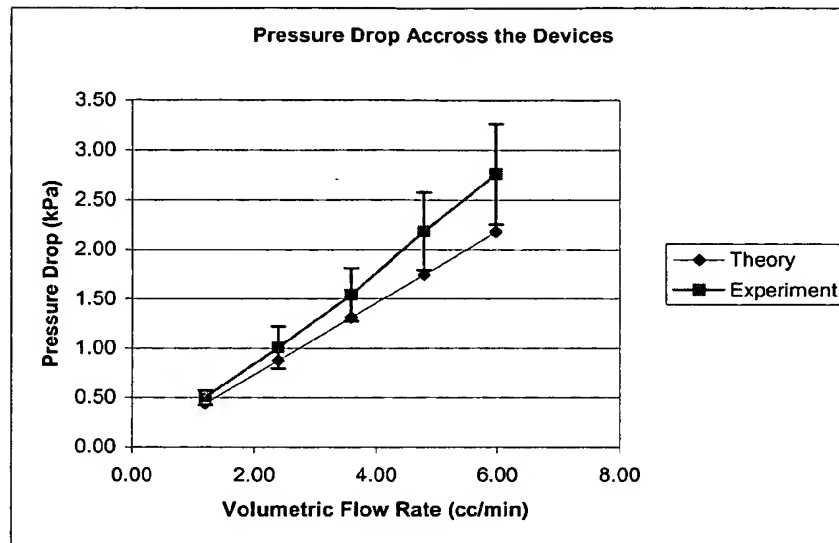


Fig. 23

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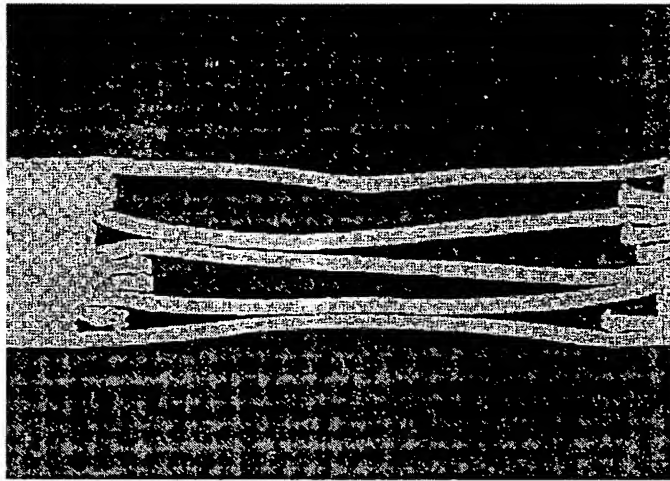


Fig. 24

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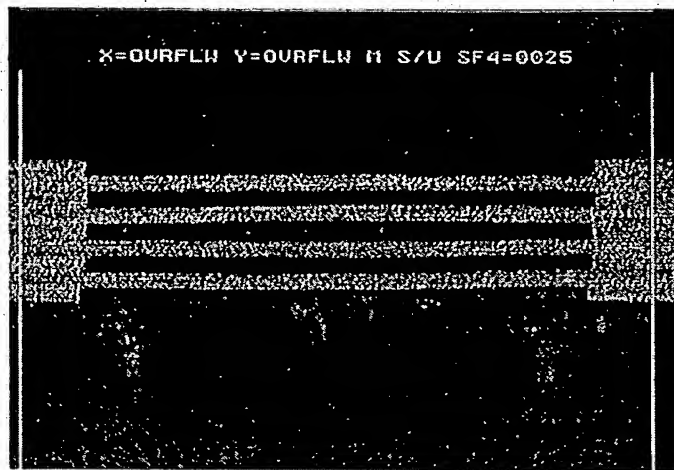


Fig. 25

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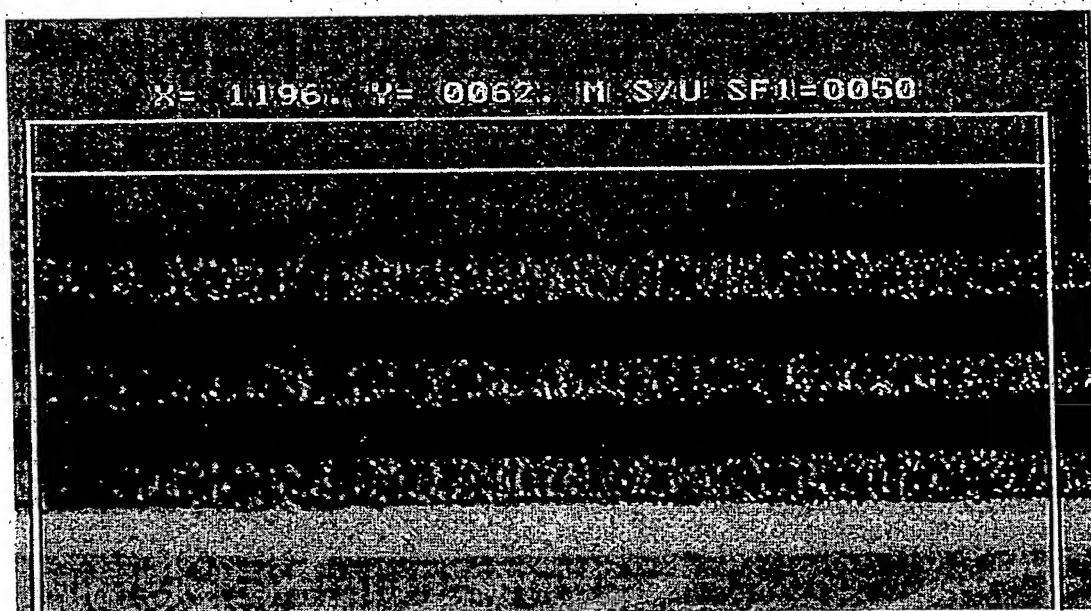


Fig. 26

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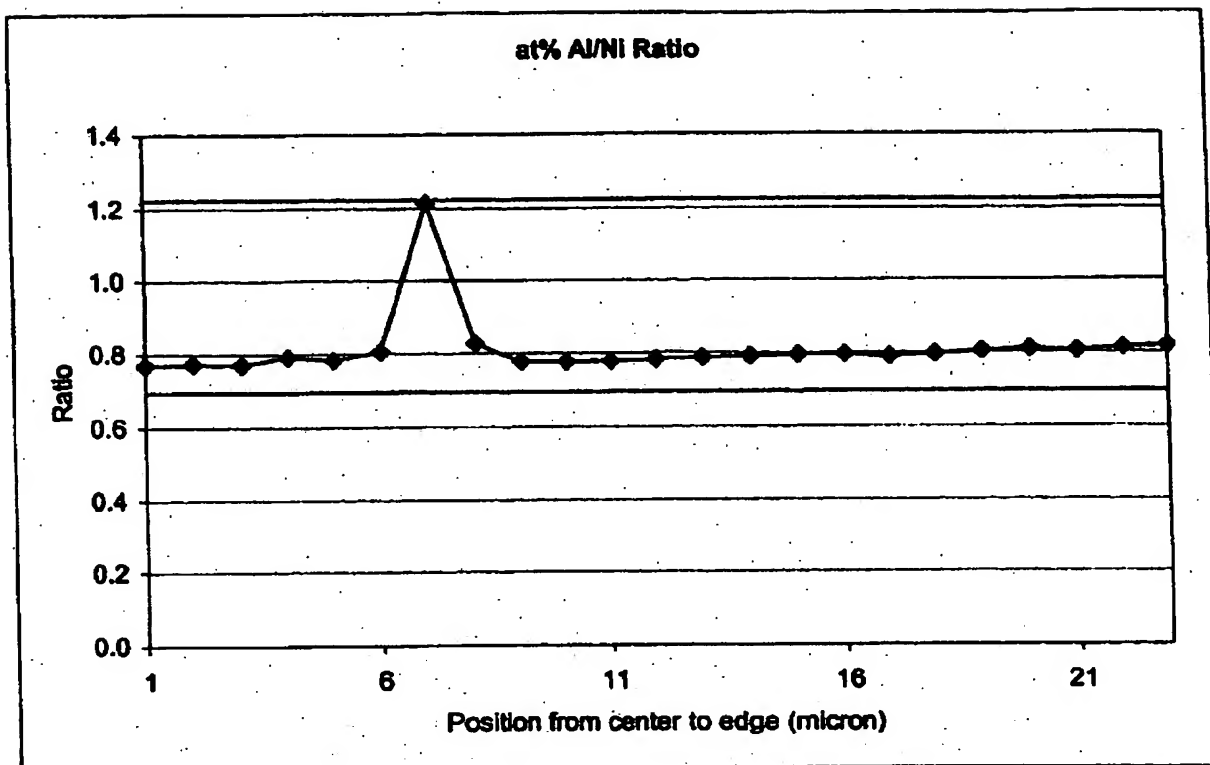
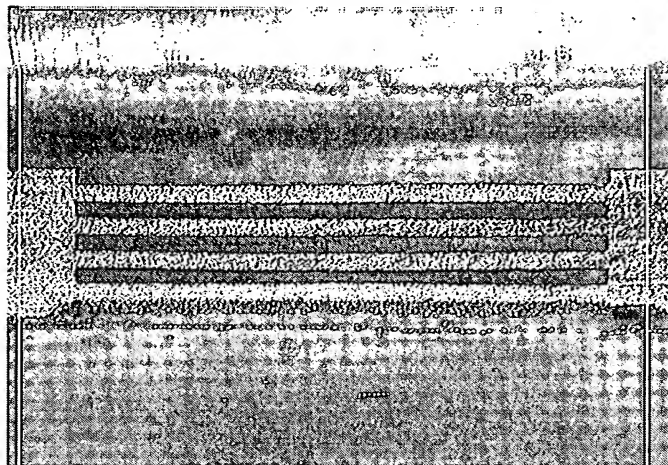


Fig. 27

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**Fig. 28**



**COMBINED DECLARATION AND POWER OF ATTORNEY  
FOR PATENT APPLICATION**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am an original, first and joint inventor of the subject matter which is claimed and for which a patent is sought on the invention entitled METHOD FOR MAKING DEVICES HAVING INTERMETALLIC STRUCTURES AND INTERMETALLIC DEVICES MADE THEREBY, the specification of which is attached hereto.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. § 1.56. If this is a continuation-in-part application filed under the conditions specified in 35 U.S.C. § 120 which discloses claims and subject matter in addition to that disclosed in the prior copending application, I further acknowledge the duty to disclose material information as defined in 37 C.F.R. § 1.56 which occurred between the filing date of the prior application and the national or PCT international filing date of the continuation-in-part application.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) of any foreign application(s) for patent or inventor's certificate or of any PCT international application(s) designating at least one country other than the United States of America listed below and have also identified below any foreign application(s) for patent or inventor's certificate or any PCT international application(s) designating at least one country other than the United States of America filed by me on the same subject matter having a filing date before that of the application(s) on which priority is claimed:

Number	Country	Day/Month/Year Filed	Claim Priority?
			<input type="checkbox"/> Yes <input type="checkbox"/> No

I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States provisional application(s) listed below:

Application Number	Filing Date
60/455,735	3/17/2003

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s) or § 365(c) of any PCT international application(s) designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, § 1.56(a) which occurred between the filing date of the prior application and the national or PCT international filing date of this application:

Application Number	Filing Date	Status: patented, pending, abandoned
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I hereby appoint the practitioners associated with the customer number provided below to prosecute this application, to file a corresponding international application, and to transact all business in the Patent and Trademark Office connected therewith:

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**Citizenship:** United States

**Inventor's Signature** \_\_\_\_\_ **Date** \_\_\_\_\_

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**Residence:** Corvallis, OR

**Mailing Address:** Corvallis, OR

**Citizenship:** Japan

**Inventor's Signature** \_\_\_\_\_ **Date** \_\_\_\_\_

**Name of Third Inventor:** Richard Dean Wilson

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**Citizenship:** United States

**Inventor's Signature** \_\_\_\_\_

**Date** \_\_\_\_\_

**Name of Third Inventor:** David Eli Alman

**Residence:** Salem, OR

**Mailing Address:** 2120 Red Oak Drive, South #36  
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**Citizenship:** United States

**Inventor's Signature** \_\_\_\_\_

**Date** \_\_\_\_\_